Fabrication, characterization and simulation of non-lithographic nanostructures and their potential applications

Neelanjan Bhattacharya
University of Nevada, Las Vegas

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FABRICATION, CHARACTERIZATION AND SIMULATION OF
NON-LITHOGRAPHIC NANOSTRUCTURES AND THEIR
POTENTIAL APPLICATIONS

by

Neelanjan Bhattacharya

Master of Science
Pennsylvania State University
2005

A dissertation submitted in partial fulfillment
of the requirements for the

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Department of Electrical and Computer Engineering
Howard R. Hughes College of Engineering

Graduate College
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We recommend that the dissertation prepared under our supervision by

Neelanjan Bhattacharya

entitled

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be accepted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Electrical Engineering

Biswajit Das, Committee Chair
Yingtao Jiang, Committee Member
Mei Yang, Committee Member
Yoohwan Kim, Committee Member
Pradip Bhowmik, Graduate Faculty Representative

Ronald Smith, Ph. D., Vice President for Research and Graduate Studies
and Dean of the Graduate College

August 2010
ABSTRACT

Fabrication, Characterization and Simulation of Non-Lithographic Nanostructures and Their Potential Applications

by

Neelanjan Bhattacharya

Dr. Biswajit Das, Examination committee chair
Professor, Electrical and Computer Engineering
University of Nevada, Las Vegas

The dissertation describes the formation of porous silicon through the pores of porous alumina on a silicon substrate. Porous silicon, by itself, is inherently a non-uniform material that has non-uniform optical and electronic properties. In addition, it is also mechanically fragile material requiring careful material handling. The porous silicon fabricated through the nanosized pores of porous alumina are expected to mitigate these problems, thereby enhancing commercial viability of the device. The porous silicon as well the porous alumina have been synthesized through anodisation for various parameters and also various types of anodizing electrolytes. The porous silicon, so obtained have been characterized through photoluminescence and Scanning Electron Microscopy. Further, applications of electropolished porous silicon, synthesized through the pores of porous alumina, as an anti-reflecting coating has been studied. The dissertation also studies the pulsed anodisation to synthesize thin film porous alumina with modulated diameters and their applications. Finally the dissertation also studies the simulations for the Surface enhanced Raman scattering in metal nanoparticles.
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CHAPTER 1
INTRODUCTION

Nanoporous materials such as porous alumina and porous silicon have attracted immense interest because of their possibility to be used in various devices. Chapter 2 of this dissertation is dedicated to the synthesis of porous silicon through porous alumina and its impact on device performance. This chapter studies application of various nanoporous materials such as porous alumina and silicon for various nanotechnology based devices. Porous silicon is a promising material and it has been used for several device applications, including electronic, photonic, sensing, and electromagnetic shielding. The conventional method of forming porous silicon is formed by the anodization of single-crystal silicon and the structure so formed consists of an interconnected network of nanoscale silicon structures. However, many problems have prevented its application in commercial devices. For instance, porous silicon is inherently a non-uniform material that has non-uniform optical and electronic properties. In addition, it is also a mechanically fragile material requiring careful material handling. While a number of devices based on porous silicon have been proposed and demonstrated, their applications have been limited by the material’s non-uniform properties and its fragile nature. Therefore one of the objectives of this dissertation is to form porous silicon through the pores of porous alumina to improve its properties. This dissertation also involves the study of various nanoporous materials and their applications in several devices.

The next problem we study is synthesis of modulated pore diameters using alternative cycles of mild and hard anodization. Chapter 3 studies this phenomena. The key concept of pulsed anodisation is to use a low voltage pulse $U_{MA}$ ("which has been called mild
anodisation”) for time interval $T_{MA}$ followed by a low voltage pulse $U_{HA}$ (“which has been called mild anodisation”) for time interval $T_{HA}$ (“which has been called “hard anodisation”). Hard anodisation produces lower porosity while mild anodisation produces higher porosity. The voltages $U_{MA}$ and $U_{HA}$ are so chosen that the cell size is same for one cycle. The voltage $U_{MA}$ usually is 25 V for sulfuric, 40 V for oxalic acid and 195 V for phosphoric acid. At these voltages in bulk material, the most well-ordered pores result.

The objective of Chapter 3 is to investigate process control for modulated pores. It has been found that apart from voltage, current density is another factor that affects cell size formation. It is extremely important to maintain cell size for MA as well as HA so that pores do not branch out and get messed up. Further for HA, current reduces exponentially with time whereas in MA the current remains constant. The current density must therefore be maintained within a certain range to match the cell size. Therefore HA pulse must be short enough so that current density drop is not much and cell size remains same. All the various process parameters for obtaining the perfect modulated pores have been detailed and explained in Chapter 3.

We have followed the recipe given by Gosele [6] for the choice of parameters. All the data reported was for bulk materials. Our report is the first report on thin film alumina on silicon substrates. Interestingly, we observed a trend where majority of pores (about 60-70%) are wider at the bottom and narrower at the top. In case of thin film, there are two key parameters which change the picture. The aluminum layer lies on tantalum, which in turn is on silicon wafer. There are lattice mismatches which produce stresses and alter the behavior of pores. The second factor is the thickness of the aluminum anodized is barely a micron, which is several orders of magnitude lower than a bulk sheet. Interesting and
novel effects of thin film make the study interesting. By inserting intermediate layers in the thin film structure, we might be able to alter the lattice stress and build interesting structures.

A reproducible trend of pores wider at top than at bottom is observed. The general trend is observed for at least 70% of pores. About 20 pores have been analysed from randomly picked areas of a sample and also from different samples. In all cases, the trends are similar. Since pore dynamics in thin films are strongly governed by lattice misfit effects due to the Si/Ta/Al structure, variations in the structure might produce interesting effects.

Chapter 4 studies simulations for synthesis of nanoparticles using plasma gas condensation and their optical characterization using Raman spectroscopy. The model proposed by Hihara is used to simulate the process control and their influence on cluster size. The various parameters studied are gas flow rate, sputtering power and length of aggregation region. Raman scattered photon carries a fingerprint of the material causing the scattering. A major bottleneck in building devices using Raman scattering for various sensors has been the extremely weak Raman signal intensity. During 1970s, certain researchers observed a dramatic increase in Raman intensity on a certain organic molecule pyridine adsorbed on roughened silver substrate. The enhancement was over a billion times, which injected a new life in Raman spectroscopy research. The enhancement occurred when the roughness of silver surface was on nanoscale range. Theoreticians explained two mechanisms- a chemical interaction mechanism leading to charge transfer between the nanoscale metal and the Raman active molecule such as pyridine. Another parallel mechanism, which holds good even if there exist no chemical
interaction and only weak Van der waals force between the metal and Raman active material. As per this mechanism, which is the basis of the simulation here, due to electromagnetic interaction between the metal and raman active material, certain hotspots are formed where the electric field is dramatically increased. These hotspots cause a dramatic increase in Raman intensity.

SERS has remained primarily a research tool due to several bottlenecks such as temporal instability and lack of reproducible data. NNC has already solved the first problem. The usual metal nanoparticles, which facilitate 3 dimensional light matter interaction are made by nanoparticles capped with surfactants, and also in colloidal solutions. While the surfactants destroy the Raman intensity, the solution based synthesis are not stable beyond a few days rendering them unsuitable for device applications. NNC has already demonstrated nanoparticles of copper on silicon substrate. These nanoparticles are stable and remain intact as long as possible, which is a key bottleneck from solving the temporal stability. Secondly a key requirement for SERS is large size nanoparticle, which can be done conveniently by NNC and has yet remained a bottleneck for chemical colloidal synthesis.

This report gives the Raman simulation of Silicon nanoparticles from a bulk like behavior to nanoparticle like behavior, which is obtained as the size of the quantum dot reduces. We simulate the first order Raman spectrum as per the calculation done by ref (11). However there is hardly any data on quantum dots. All the theories developed are for quantum dots embedded in matrix since experimentalists have typically made such type of quantum dots. The Raman spectra from bulk silicon has an LO-phonon peak at 520 cm$^{-1}$ and is a lorentzian curve with a FWHM=4.7 cm$^{-1}$. In bulk materials, only the
phonons at the center of the Brillouin zone contribute to Raman intensity as per the rules of momentum conservation. At the nanoparticle level, the phonons are confined within the nanoparticles and phonons away from the zone center, extending up to the edge of brillouin zone contribute to Raman scattering. Due to the participation of these phonons, the Raman spectra broadens and the peak shifts. The spectra also becomes asymmetric due to the nature of the phonon dispersion curves of silicon, which has negative gradient.

Chapter 4 investigates the size dependence on Raman scattering broadening and asymmetry due to quantum confinement effects. Our simulated data is in good agreement with usual trends. However our nanoparticles are free standing and the theoretical calculation is for nanoparticles in a matrix. We expect a deviation from the calculation and the degree of deviation will be interesting quantity to investigate. At the same time our size controlled manufacturing will give a realistic estimate of the broadening. When the nanoparticle size varies, the broadening reported is far in excess of theoretical calculations.
CHAPTER 2

FABRICATION OF POROUS SILICON THROUGH NANOSCALE PORES OF THIN FILM ALUMINA AND THEIR APPLICATION TO SOLAR CELLS

This chapter studies the fabrication of porous silicon through pores of porous alumina. The details of the fabrication and characterization are described in sections below.

2.1 Choice of wafers and ultrasonic cleaning

Three types of silicon wafers were studied: p type, p++ and n type. For p++ type, the resistivity was 0.001-0.005 ohm cm, for p-type wafers the resistivity was 0.53 ohm cm and for n type, the resistivity was 1-20 ohm cm. The thickness of the p++ wafer was 0.53 mm, that of the p type was 0.75 mm and that of n type was 0.3 mm. The wafers were cleaned for about 2 hours in a sonicator bath and were immersed in a solution of acetone, ethanol and methanol. The sonicator bath was set to produce ultrasonic oscillations at 25 kHz as well as 45 kHz. Various modes such as “normal”, “sweep” and “degas” were used to thoroughly clean the wafers. After cleaning in the organic solvents, the wafers were dipped in 1.5% HF solution for a few seconds to remove the native oxide. The wafers were then dried for a couple of hours.

2.2 Electron beam evaporation of aluminum

Electron Beam Evaporation a form of physical vapor deposition in which the target, which is the material that must be deposited, is made anode and it is then subjected to an electron beam emitted by a cathode, which can be of various types as per the need. The electron beam given off by a cathode. The cathode is typically a charged tungsten filament and is maintained under high vacuum. The electron beam causes atoms from the
target to transform into the gaseous phase. These atoms then deposit on the target, steadily condense into solid thin film. Electron beam evaporation is in particular problematic due to several reasons.

Molten Aluminum excessively wets crucible liner. This causes molten aluminum to swell up, come out of the crucible liner and spill out. If this happens, the solidified Al has to be removed with a screwdriver. Aluminum has a tendency to escape the hot area, where the e-beam hits, and accumulate at colder areas. If the e-beam is fixed and incident at the center of the crucible liner, this leads to a concave surface and non-uniform temperature gradient. This tendency is avoided by sweeping the e-beam all over the crucible in the form of a pattern, such as "8" and doing some parameter control. Aluminum contracts at a rate 20 times the crucible material. This causes 80% crucibles to crack at temp about 250C. This problem was avoided by very gradually cooling the crucible, and sweeping the e-beam.

In regard to Aluminum evaporation, several following precautions must be followed. Since aluminum has a tendency to creep up the walls and flood out, fill the crucible no more than halfway with material. The amount should be such that the crucible surface is not exposed to electron beam, and just enough aluminum pellets are used. Use small size aluminum pellets to mitigate this problem. Bring the power up slowly and bring it down slowly. Spend time ramping up and down, otherwise the crucible could crack. Allow the material and crucible time to cool down after run.

The achievements of first run were the e-beam sweep was done successfully. We saw crucible did not develop even a small scratch. It was intact. No degradation observed, as the crucible cooled from 1500C to room temp. This is the most encouraging thing, which
indicates that e-beam sweep and gradual cooling helps to reduce thermal stress. The deposition rate for the first run was at 0.2 Ang/sec. Of course 20nm is not a reasonable target and is barely discernible. But the interesting thing is 0.2Angs/sec deposition rate was achieved at lower currents of 40 mA with e-beam sweep. No spillage of Al was observed. However the surface of Al has some concavity. There are ways to mitigate this. The e-beam sweep helps to sweep the e-beam all over the crucible liner uniform and well.

2.3 Formation of thin film porous alumina

If aluminum metal is immersed in certain electrolytes as the anode and a current is passed between anode and cathode, electrochemical oxidation of aluminum occurs. The anodized aluminum consists of hexagonal pattern of cells in the form of pillar like structure. A picture of top view and cross section of a porous alumina template is shown below. The top view consists of hexagonal regularly arranged array network of cells with circular holes at the center. The cross section is shown alongside clearly showing a pillar like structure. The size of the region between two such holes is called cell wall and each hexagonal unit with a hole in the center is called a cell. The diameter of the pores depend on the process parameters such as pH of electrolyte, electrical parameters such as magnitude of applied voltage or current density used type of anodizing electrolyte. It is found that certain acids like sulfuric acid, oxalic acid, phosphoric acids cause simultaneous oxidation and dissolution of the aluminum oxide producing a hexagonal nanoporous structure, while certain acids like citric acid and boric acid produce a dense nonporous layer of aluminum oxide.

Porous alumina, thus formed by electrochemical oxidation of aluminum, has a number
of interesting applications because of its symmetric hexagonal structure. While porous alumina has several advantages, it has several disadvantages. It is inherently fragile material and difficult to be incorporated into silicon technology. To mitigate this problem, Nevada Nanotechnology Center has created a sample holder to implement anodisation of thin film aluminum on silicon substrate.

Figure 2-1 Top view of porous alumina template
Figure 2-2 cross section view of porous alumina template

The thin film anodisation is implemented using sample holder as shown below. Inside the sample holder, an o-ring made of compressible material is placed first, then a sample of size about 1cm x 1cm is put, followed by a compression spring then a metal disc is put. Then a cap, which is threaded in to the plastic enclosure is put at the back. In this way, thin film aluminum can be anodized on a silicon substrate.

The anodisation facility at Nevada Nanotechnology is computer controlled and has several interesting features. A double walled container is used to contain the anode and cathode. A kepco power supply 500M BOP model type is used for providing constant current or constant voltage anodisation. The voltage drive can be up to 500V and current current drive up to 80mA.
Compression spring

Ø 0.93” inner diameter of plastic enclosure

Ø 0.805” outer diameter of metallic cylinder

0.26”

0.58”

0.8”

0.35”

0.1”

Ø 3/32” O-ring

metallic cylinder of 1/16” thickness.

Figure 2-3   A cross sectional view of the sample holder
Using LABVIEW, the voltage developed between anode and cathode can be displayed and saved. A typical voltage-time graph is displayed below. Initially, the voltage is developed linearly with time. This corresponds to formation of “barrier oxide”. Afterwards, it reaches a peak and then starts dropping. At this step, the pores just nucleate and start forming on the top surface of the film. The pores grow in size and as per the process parameters, attain an equilibrium size. The voltage continues to decrease during phase, and this phase is called “pore propagation” phase. The next phase is called “pore propagation phase”. During this phase, the pores propagate vertically downwards. The voltage developed remains more or less constant and the plateau in the graph indicates this region. The last phase is the period when the pores propagate down to the bottom, eventually reaching the silicon substrate and rapidly start oxidizing the silicon into silicon.
dioxide. This phase is indicated by the rapid rise of voltage in the graph.

Figure 2-5 Graph showing typical stages of anodisation.
Figure 2-6 Top view of SEM images of porous anodic alumina.
Figure 2-7 cross section view of SEM images of porous anodic alumina.
2.4 Porous silicon formation

As the name suggests, porous silicon is a form of the element silicon with a large number of pores. Porous silicon is formed by the anodization of single-crystal silicon and consists of an interconnected network of nanoscale silicon structures. The pore sizes can range from micron to nanometer size range. The most promising property of porous silicon is its capacity to efficiently absorb and emit light. Porous silicon is a very interesting material and has been proposed for a range of several device applications, which range from electronic, photonic, sensing, electromagnetic shielding, explosive (due to the ease with which oxygen can react with the high surface area) and even providing thrust to satellites.

Porous silicon can be formed by several methods and the most common method is known as “anodisation”. “Anodisation” is essentially electrolysis, but for porous silicon the electrolyte used is hydrofluoric acid. A silicon wafer is used as anode and a platinum mesh typically is used as cathode. When electric current is passed from the anode to the cathode through the electrolyte, the hydrofluoric acid starts corroding the silicon wafer causing a structure of holes to be formed all over the silicon wafer. The reaction of hydrofluoric acid with silicon produces a lot of hydrogen gas evolution, which can interfere with the capacity of hydrofluoric acid to penetrate the pores. This leads to non uniform dissolution of silicon and degrades porous silicon formation. To mitigate the hydrogen evolution problem, ethanol must be added to the HF.

Conventional porous silicon, as an efficient light emitter is made under relatively low current density, such as 5- 50 mA/cm². At high current densities, typically, greater than 120mA/ cm², a phenomenon known as “electropolishing occurs”. In this phenomenon,
the surface of the silicon gets etched and the sample looks very dark. This has very interesting applications in solar cells, such as “antireflection coating” in solar cells.

Porous silicon synthesis utilizes hydrofluoric acid as electrolyte. Hydrofluoric acid is one of the most corrosive acids and needs very high degree of caution. There are few substances that are not affected by it. Among plastics, Teflon is HF inert, among compressible polymers, neoprene and among metals platinum, silver and gold can withstand HF. Therefore to perform synthesis in HF, a new sample holder made of high quality Teflon was fabricated. The O-ring was made custom made from sheets of neoprene. A stainless steel plate was used wherever metal plate was needed. An image of the sample holder specially fabricated for porous silicon synthesis is shown below. However, porous silicon is inherently a non-uniform material that has non-uniform optical and electronic properties. In addition, it is also mechanically fragile material requiring careful material handling. While a number of devices based on porous silicon have been proposed and demonstrated, their applications have been limited by the material’s non-uniform properties and its fragile nature. If the material uniformity and mechanical integrity of porous silicon can be improved, it can increase the potential for commercial applications of this material. Towards this goal, we have fabricated porous silicon by anodization through an electrochemically formed porous alumina template on a silicon substrate.
2.5 Porous silicon through alumina

The fabrication technique is schematically shown in Fig. 1. A porous alumina template is first created on the silicon substrate by anodizing a thin film of aluminum deposited on the substrate. Next, porous silicon is formed through the template pores. The pores in the template are then sealed using a simple hydrolysis step to form a protective coating on the porous silicon layer.

Figure 2-8 Flowchart showing process flow for device design.
Figure 2-9 The wafers must be cleaned and aluminum must be deposited front and back.

Figure 2-10 Porous Alumina is then formed electrochemically by anodisation.
Figure 2-11 Then there is pore widening in phosphoric acid, followed by porous silicon formation through the pores of porous alumina through a second anodisation step.
Figure 2-12 Then the pores of porous alumina are sealed by a hydrolysis steps, which involves boiling in DI water.
Figure 2-13 Now, the same process flow is repeated with a different anodizing electrolyte for porous alumina, oxalic acid. The pores are bigger than sulfuric acid.
Figure 2-14 now phosphoric acid is used as anodizing electrolyte, and wider pores are formed.
2.6 Parameter control different acids

The objective of this thesis is to study formation of porous silicon through porous alumina for various parameters. The emphasis is on process control of the porous alumina layer. With this objective, we used different acids for anodisation. Sulfuric acid at 20% wt. concentration, oxalic acid at 0.4M wt. concentration and phosphoric acid at 10% wt. concentration were used as anodizing electrolytes. Sulphuric acid typically causes pores in the 10-40nm range, oxalic acid typically causes pores in the 80-120nm range and phosphoric acid causes really large pores typically greater than 100nm. The spacing between pores or cell width also varies as the acid is changed.

2.7 Electropolished porous silicon and its application to solar cells

The device discussed in this dissertation, which involves porous silicon synthesis through the pores of porous alumina has an interesting application to solar cells. The device will be used as antireflection coating in solar cells. The porous silicon has been electropolished by applying a current density of 100mA/cm². The electropolishing process etches the silicon surface making it very rough and this produces a textured surface. We propose an electropolished porous silicon through porous alumina to be used as antireflection coating in solar cells. The alumina cap acts as a protective coat, thereby enhancing commercial viability of the device. The samples were imaged using JEOL 7500 FESEM. The top view of the aluminum template, which seemed to have got somewhat etched due to electrochemical dissolution in hydrofluoric acid is also shown. Nevertheless for a time of anodisation= 45 seconds, some alumina definitely survives. The cross section images of the same sample were obtained using JEOL FESEM 7500.
and are shown in figure below. There are three distinct layers, the bulk silicon at the bottom, followed by porous silicon at the top and porous alumina at the top.

Figure 2-15  A schematic picture of the proposed device to be used as antireflection coating in solar cells.
Figure 2-16 SEM image showing top view of electropolished porous silicon through porous alumina.
Figure 2-17 SEM image showing cross section of electropolished porous silicon through porous alumina.
2.8 Photoluminescence characterization

Photoluminescence characterization is one of the most straightforward types of optical characterization of materials. In this phenomenon, a material absorbs photons and reradiates photons. In terms of quantum mechanical theory, this can be described as excitation to a higher energy state and then return to a lower energy state, accompanied by release of photon. The period between absorption and emission is typically extremely short, in the order of few nanoseconds. Upon absorbing photons, the electrons are moved up to “metastable” states, wherein they stay for very short interval of time before collapsing back to the ground state. Therefore photoluminescence is a good way of measuring the bandgap.

![Figure 2-18 Sketch showing concept of photoluminescence](image)

The source of excitation can be any laser whose photon energy exceeds the bandgap of the material to be examined, and whose power is sufficient to excite an adequate signal. Many commercial types of laser including HeNe and Ar+ lasers meet this criteria. In case of porous silicon, typically the emission peak lies in the visible-NIR region, ranging
from 650 to 750nm. For the samples manufactured in the laboratory, the emission peak was in the NIR region from 700-720nm. Therefore, a laser source, in the form of a laser pointer, lasing at deep blue-UV transition region of 407nm and power 20mW was used to excite photoluminescence. The criteria for laser power is such that it must be enough to excite a signal but laser power cannot be increased indefinitely. Too high an intensity can cause non linear effects and a focused laser spot may also damage the sample. Therefore, a sufficient value of signal to ratio needs to be obtained by defocusing the laser or reducing its output power. In the porous silicon experiments studied, 20mW power was used, however the laser spot about a few millimeters in diameter was made to directly be incident on the sample, without any focusing optics between the laser and the sample.

The laser was then mounted on chemistry stands so that the light is incident on the sample. The whole setup was enclosed in an enclosure to prevent noise signals from atmosphere from corrupting the useful signal emitted by the experimental samples. A long working distance objective lens of magnification 10X was used in the microscope to collect the light emitted the porous silicon. The working distance was several centimeters long and therefore facilitated the laser light to be incident on the sample.

After being collected by the objective lens, the light is further collimated. A beam splitter and heat absorbing light were placed in the appropriate slots for the filters. These filters absorbed the IR noise and allowed the useful signal from the sample to get into the grating monochromator. The Labspec software was used to program the computer controlled data acquisition and the grating was selected at 600 lines/cm by using this
software. The software also has the provision to set the exposure time on the detector, and number of accumulations. A set of “2” is recommended to measure reliable data. A silicon CCD Andor thermoelectrically cooled detector was used to detect the signals. The detector temperature during measurement was about -65°C and was attained in a few minutes after software startup.

Figure 2-19 An image of the HORIBA LABRAM HR800 setup to measure photoluminescence.
Fig 2-20 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current \(36\text{mA/cm}^2\) for porous alumina and anodized in HF at constant current \(45\text{mA/cm}^2\). The spectra was measured for a point on the edge of the sample.
Fig 2-21 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36mA/cm$^2$ for porous alumina and anodized in HF at constant current 45 mA/cm$^2$. The spectra was measured for a point on the center of the sample.
Fig 2-22  Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36mA/cm² for porous alumina and anodized in HF at pulsed current 45 mA/cm² at 1KHz 50% duty cycle. The spectra was measured for a point on the edge of the sample.
Figure 2-23 - Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36mA/cm² for porous alumina and anodized in HF at pulsed current 45 mA/cm² at 1KHz 50% duty cycle. The spectra was measured for a point on the center of the sample.
Fig 2-24 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36mA/cm² for porous alumina and anodized in HF at pulsed current 45 mA/cm² at 1KHz 33% duty cycle. The spectra was measured for a point on the edge of the sample.
Fig 2-25 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36mA/cm² for porous alumina and anodized in HF at pulsed current 45 mA/cm² at 1KHz 33% duty cycle. The spectra was measured for a point on the center of the sample.
Fig 2-26 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36mA/cm² for porous alumina and anodized in HF at pulsed current 45 mA/cm² at 10Hz 50% duty cycle. The spectra was measured for a point on the edge of the sample.
Fig 2-27 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36 mA/cm² for porous alumina and anodized in HF at pulsed current 45 mA/cm² at 10Hz 50% duty cycle. The spectra was measured for a point on the center of the sample.
Fig 2-28 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36 mA/cm² for porous alumina and anodized in HF at pulsed current 45 mA/cm² at 10 Hz 33% duty cycle. The spectra was measured for a point on the edge of the sample.
Figure 2-29 Photoluminescence spectra of a sample anodized in sulfuric acid at constant current 36 mA/cm$^2$ for porous alumina and anodized in HF at pulsed current 45 mA/cm$^2$ at 10 Hz 33% duty cycle. The spectra was measured for a point on the center of the sample.
3.1 Pulsed anodisation roadmap

The previous reports explained and showed the pulse profiles obtained. In this report a roadmap to pulsed anodisation in order to obtain modulated pore diameters is explained. The key concept of pulsed anodisation is to use a low voltage pulse $U_{\text{MA}}$ (“which has been called mild anodisation”) for time interval $T_{\text{MA}}$ followed by a low voltage pulse $U_{\text{HA}}$ (“which has been called mild anodisation”) for time interval $T_{\text{HA}}$ (“which has been called “hard anodisation”). Hard anodisation produces lower porosity while Mild anodisation produces higher porosity. The voltages $U_{\text{MA}}$ and $U_{\text{HA}}$ are so chosen that the cell size is same for one cycle. The voltage $U_{\text{MA}}$ usually is 25V for sulfuric, 40V for oxalic acid and 195V for phosphoric acid. At these voltages in bulk material, the most well ordered pores result.

Now we need to decide how to choose the times. It has been found that apart from voltage, current density is another factor that affects cell size formation. It is extremely important to maintain cell size for MA as well as HA so that pores do not branch out and get messed up. Further for HA, current reduces exponentially with time whereas in MA the current remains constant. The current density must therefore be maintained within a certain range to match the cell size. Therefore HA pulse must be short enough so that current density drop is not much and cell size remains same. A short duration HA pulse helps to reduces joule heating, which can cause burning. Therefore based on these conditions we will choose HA pulse width. In case of MA pulse width, it has been found
that HA pulses often produce a dense barrier oxide, due to which current during MA dies out after a few cycles. The duration of MA should be long enough to allow MA current to catch up to a value necessary to maintain the cell size. So, the roadmap will be:

1) On the Si /Ta/Al samples, we will make templates to obtain the most well ordered voltage range, to obtain our MA range for “thin films”. The thin film ordering will be worse than bulk but we will try how far we can go.

2) We first tabulate how cell size, porosity, pore size and oxide growth rate occurs for MA.

3) We repeat these steps for HA to obtain what voltage ranges to choose

4) The times and voltages for MA and HA will be chosen as per the consideration above.

5) We first manually do MA, stop anodisation, observe the images, and then do HA and again observe the images.

6) We test different acids to see where we get best results.

Therefore we need to make several templates and images them to compare the MA-HA phenomena in thin films.

### 3.2 I-V graphs for modulated pore diameters

The I-V graphs for modulated pore diameter formation are explained in this report. The main concept used by Gosele is- in order to get modulated pores, anodize under two conditions- “mild anodisation”, followed by “hard anodisation”. Mild anodisation is usually performed at lower voltages about 40V for oxalic acid and results in pores with a certain pore size and a certain cell size. In mild anodisation, the oxide growth rate is very slow. The other anodisation condition is “hard anodisation”, where the oxide growth rate
is much faster. This type of anodisation is usually performed at higher volts eg >110V for oxalic acid. This results in formation of pores again with a certain pore size and a certain cell size. One period of the modulated pore diameter consists of a half cycle of mild anodisation followed by another half cycle of hard anodisation. The parameters- acid conc and voltage must be selected so that the cell size remains same. Due to the inherent nature of hard anodisation, the pore size for hard anodisation is smaller than mild anodisation resulting in modulated pores. The cell size depends on- voltage applied, acid conc and current density. We started the experiment by performing constant voltage anodisation at 0.3M oxalic acid conc at different values of voltage, as the graphs in fig 3-8 indicate. In fig 3a the anodisation was done at 40V and 0.3M conc. We waited as long as 200sec, but Ta wasn’t yet touched. We stopped the anodisation and then resumed as in fig 3b till about 120sec. So it took as long as 320 sec to oxidize 750nm of Al. Now we next moved to 50V, where it took as much as 450-500 sec to oxidize Al. So this is the mild anodisation regime. In fig 5, it takes about 150 sec, note that the voltage changed from 70 to 50, marginally, but the time to oxidize, drastically fell down to 100 sec range, indicating onset of hard anodisation. In fig 6, for 90V, it took just about 30 sec to oxidize. Now, at 110-120V in fig 7 and 8, the oxidation was almost instant, may be about 5-6sec range. Observe the drastic time scale difference. From 300-500 sec at mild anodisation corresponding to 5-6 sec at hard anodisation at 110V range. Thus we may assume 40-50V to be “mild anodisation range” and “70- 110V” to be in hard anodisation range. Note that there is a drastic difference in current densities for HA and MA at the same conc. Such a large difference in current density will give different cell sizes and that will destroy modulated pore structure. Based on this rationale (suggested by gosele),
we reduced the acid conc to 0.1M and performed HA keeping high voltage and attain a comparable current density. Graphs 9-12 indicate the 0.1M condition. For 50V the current was about 8mA and for 40V current was about 4mA. We observe from fig 11 and 12 that between 100-130V range we expect about 8-9mA current. Based on this rationale, parameter chosen was 50V 0.3M for “MA” half cycle and 115V 0.1M for “HA” half cycle. For this final sample, refer to fig 1a and 1b for the MA and HA half cycle graphs. We prepared another sample with MA at 0.3M 40V and current attained was 3-4mA. At 0.1M, we found at 70-90V range, the current attained is comparable to 3-4mA as shown in fig 9. Therefore another sample no 2 was prepared with MA cycle parameters as 0.3M-40V and HA cycle as 0.1M-70V as well as 0.1M-90V.

3.3 Microscopic characterization of modulated pore diameters of thin film nanoporous alumina deposited on silicon substrates

In order to build multispectral detectors and solar cells, it is useful to build modulated pores. This report summarizes the SEM data analysis of the pores which were anodized in oxalic acid two cycles with two different parameters. The Current time graphs were analyzed in the previous section and may be obtained from there. Four samples were prepared and the images of each sample are analyzed below. The top view as well as cross section was obtained in each case. For the first sample, the parameters chosen was 0.3M/40V/140sec for the first cycle and 0.1M/70V/70sec for the second cycle. We have followed the recipe given by Gosele[1] for the choice of parameters. Gosele[1] had obtained pores which are wider at the top and narrow at the bottom. This is because the parameters for first half cycle correspond to mild anodisation, where pores with smaller
size are formed whereas second half cycle corresponds to hard anodisation, where pores of bigger size are formed. All the data reported was for bulk materials. Our report is the first report on thin film alumina on silicon substrates.

Interestingly, we observed a trend where majority of pores (about 60-70%) are wider at the bottom and narrower at the top. In case of thin film, there are two key parameters which change the picture. The aluminum layer lies on tantalum, which in turn is on silicon wafer. There are lattice mismatches which produce stresses and alter the behavior of pores. The second factor is the thickness of the aluminum anodized is barely a micron, which is several orders of magnitude lower than a bulk sheet. Interesting and novel effects of thin film make the study interesting. By inserting intermediate layers in the thin film structure, we might be able to alter the lattice stress and build interesting structures.

For the first sample the parameter chosen was 0.3M/40V/140sec for the first half cycle and 0.1M/90V/100sec for the second half cycle. In fig1, we show a low magnification view spanning about 10 microns. A line is drawn midway to distinguish the second half cycle from the first. The general impression from this image is pores below the line are wider than those above. The density of pores above the lines is more in than that below. Therefore many pores do not propagate for the second half cycle. Figure 1(b) shows the pore structure at 100K magnification. The pore diameter at top, middle and bottom of pores are tabulated in table1. Majority of pores about 70% are wider at bottom than at top. The average pore size is 35-55-65nm at top-middle-bottom. Pores narrow at top half and wider at bottom are distinctly observed. An image from another section of the same sample is provided in figure 1(c). The average pore size is about 17-30-40nm measured at top-middle-bottom.
The pore tapering seems to be reproducible phenomenon. In thin films, since the thickness anodized is very small, the pores do not obtain thermodynamic equilibrium and fluctuation in pore size is observed as we examine different sections of the wafer, however there is a strong reproducibility of the pore tapering trend.

Now for sample 2, the parameters chosen was 50V/0.3M/150sec for first cycle and 0.1M/115V/40sec for second cycle. The results are tabulated in table 2. In this case also, we observe about 50-60% pores are wider at bottom than at top. This seems to be a general trend and pore sizes vary from 30 to 38 nm from top to middle and more drastic variation to about 60nm. Now for third sample, parameter chosen was 45V/0.3M/100sec for first cycle and 0.1M/120V/60sec for second cycle. The higher voltage used for second stage of anodisation produces highest values of pore diameter upto about 80nm at bottom, 50nm at middle and 30nm at top. For the fourth sample also, we observe a similar trend with pore profile being about 30-50-70nm. A reproducible trend of pores wider at top than at bottom is observed. The general trend is observed for atleast 70% of pores. Pores have been analysed from randomly picked areas of a sample and from different samples.
Figure 3 –1 cross section SEM image of sample 1 showing overall pore morphology.
Figure 3–2  cross section SEM image of sample 1  for pore diameter analysis
Figure 3-3 cross section SEM image of sample 1 for pore diameter analysis
Figure 3-4  cross section SEM image of sample 2 showing overall pore morphology.
Figure 3–5  cross section SEM image of sample 2  for pore diameter analysis
Figure 3-6 cross section SEM image of sample 3 showing overall pore morphology.

Note first half of final sample 3, corresponding to mild anodisation at 45V/0.3M/100sec.

Note second half of final sample 3, corresponding to hard anodisation at 0.1M/120V/60sec
Figure 3–7  cross section SEM image of sample 3 for pore diameter analysis
Figure 3-8 cross section SEM image of sample 4 showing overall pore morphology.
Figure 3-9 cross section SEM image of sample 4 for pore diameter analysis
CHAPTER 4

SIMULATION OF PROCESS CONTROL PARAMETERS FOR SYNTHESIS OF NANOPARTICLES AND THEIR OPTICAL CHARACTERIZATION

4.1 Simulation of silicon nanocluster formation by plasma gas condensation process.

The nanodeposition system nanosys1 uses plasma gas deposition technique for synthesis of nanoparticles. The modeling for plasma gas condensation technique has been done by Hihara et al. In this section, we explain the dependence of nanocluster size with the three parameters. The simulation of the nanocluster formation for the “plasma gas condensation” process has been performed for Si nanoclusters. The model developed by Hihara et al.,[1] was used for this process. The material parameters chosen were those of Silicon for the nanocluster and for Argon in figure 1 and 2 and Helium-Argon in figure 3 and 4. In Hihara’s original paper, the drift velocity is estimated to be 0.4m/s. This value is reached if the total pressure for He-Ar mixture=280Pa is used. However since He and Ar, in a mixture, they would obey the well known dalton’s law of partial pressures and therefore the partial pressure of He should have been used which would give a higher drift velocity=0.9m/s. The fig 1 shows the cluster size as a function of aggregation length at different values of vapor density. The gas used is Argon. In figure 2, the cluster size is given in terms of diameter of nanoparticle formed in nm. In the Hihara model, vapor density is used as a free parameter and was assumed. We are trying to also simulate the magnetron sputtering behavior that will give a relation between sputtering power applied and the vapor density produced. The paper by Hihara simulates the gas dynamics only.

In figures 3 and 4 we show the simulated data for He-Ar mixture with the He gas being the predominant mode to cause the flow of the nanoclusters. The nanoparticle size
generated is essentially a function of the aggregation length and the desired aggregation length must be selected from the graph to get the desired nanoparticle. The cross section of aggregation region of our set up is assumed to be same as Hihara’s set up = 0.0014 m². More simulations are required to design the sample for Raman measurement, the choice of a substrate/coating later on Si nanoparticle etc.

Figure 4-1 variation of cluster size in terms of number of atoms with aggregation length for various vapor density in Argon ambient.
4.2 Simulation of SERS of metallic quantum dots on solid state substrates

This section details the results of simulation of absorption, scattering and extinction spectra of gold and silver nanoparticles. This is a very interesting topic because the simulation results we obtained show a wide tuning range from UV to IR which depends on material and size of nanoparticle, substrate as well as wavelength and polarization of incident radiation. There is an analogy to semiconductor dots but the underlying physics is completely different.

In comparison to semiconductor nanoparticles where the blue shift occurs due to electron/hole energy quantization to produce major modifications of their optical properties, the changes that occur with metallic nanoparticles are derived from effects that can be explained using a classical dielectric picture. Mathematically, the “Laplace” equation and “Maxwell’s” equation are solved for electric field interaction with a spherical nanoparticle subject to two boundary conditions, similar to the approach used in solving electromagnetic theory problems.

(i) Electric potential is continuous at the sphere surface
(ii) Normal component of electric displacement is also continuous.

These equations are solved to obtain “absorption peak”, “scattering peak” and “extinction peak”. The radiation incident on the sphere is partly absorbed, partly scattered and remainder may be transmitted. The extinction coefficient, which is the sum of absorption and scattering coefficient, therefore gives the total radiation intercepted by the nanoparticle and in the simulations below, we examine the wavelength at which the peaks extinction peak occurs for a range of parameters. Light absorption by metal
nanoparticles leads to coherent oscillation of electrons in the conduction band. The electron cloud gets drifted due to applied E-field of light.

When electron cloud is displaced relative to the nuclei, a restoring force arises from coulomb attraction between electrons and nuclei that results in oscillation of electron cloud relative to the nuclear framework. The collective oscillation of electrons has been termed “Plasmon resonance”. The “Plasmon resonance” occurs for a specific wavelength of light for a specific nanoparticle. The “extinction coefficient” (which is a measure of absorption and scattering strengths collectively) is calculated according to the formula

\[
k_{ex} = \frac{18\pi NV\varepsilon_m^3}{\lambda} \frac{\varepsilon_2}{[\varepsilon_1 + 2\varepsilon_h]^2 + \varepsilon_2^2}
\]

Here \(\lambda\) is the wavelength of the incident light, and \(\varepsilon_h\) is the dielectric constant of the surrounding medium. \(\varepsilon_1\) is the real part of the dielectric constant, and \(\varepsilon_2\) is the imaginary part of the dielectric constant of the metal which is given by

\[
\varepsilon_m = \varepsilon_1 + i\varepsilon_2
\]

Both \(\varepsilon_1\) and \(\varepsilon_2\) are dependent on the frequency \(w\) of the incident light. If \(\varepsilon_2\) is small or weakly dependent on \(w\), the absorption maximum corresponding to the resonance condition is produced when,

\[
\varepsilon_1 = -2\varepsilon_h
\]

This condition leads to a vanishing denominator. This is the reason why a surface plasmon resonance condition is produced at optical frequency \(w\) at which the resonance condition is fulfilled.

\[
\varepsilon_1 = -2\varepsilon_h
\]
This equation also explains why we need metal nanoparticles as they have negative dielectric constant and equation (1) can thus be satisfied for a Ag nanoparticle with negative dielectric constant on a semiconductor substrate with positive dielectric constant. The equation (1) is derived using a simple electrostatic theory, proposed by Kelly et al. As more realistic assumptions are made, deviations occur in this equation also but for introductory understanding, the above formula has been usually assumed. At the extinction peak, when the above equation is followed, we examine the electric field and observe that hotspots with very high induced electric fields are produced. The location of the hotspots depends on the parameters chosen. It is shown below that the hotspots may form the vertices of a square or are radially distributed or located along a certain axis as per the parameters chosen. We report that it is possible to tune the absorption and extinction peak from 357nm to as high as 857nm and our optimum results show that we can obtain an electric field enhancement of 773 times the incident electric field for a 15nm Silver nanoparticle on a GaAs substrate. High induced electric fields can dramatically increase the Raman signal intensity and enable detection of even a single molecule. The simulations help us to understand how SERS has been used for groundbreaking applications from drug detection to tissue imaging.

4.3 Experiment to study surface enhanced Raman spectra in gold nanoparticles.
Raman scattered photon carries a fingerprint of the material causing the scattering. A major bottleneck in building devices using Raman scattering to detect materials in sensors has been the extremely weak Raman signal intensity. During 1970s, certain news researchers observed a dramatic increase in Raman intensity on a certain organic
molecule pyridine adsorbed on roughened silver substrate. The enhancement was over a billion times, which injected a new life in Raman spectroscopy research. The enhancement occurred when the roughness of silver surface was on nanoscale range. Theoreticians explained two mechanisms- a chemical interaction mechanism leading to charge transfer between the nanoscale metal and the Raman active molecule such as pyridine. Another parallel mechanism, which holds good even if there exist no chemical interaction and only weak Van der waals force between the metal and Raman active material. As per this mechanism, which is the basis of the simulation here, due to electromagnetic interaction between the metal and raman active material, certain hotspots are formed where the electric field is dramatically increased. These hotspots cause a dramatic increase in Raman signal intensity.

SERS has remained primarily a research tool due to several bottlenecks such as temporal instability and lack of reproducible data. NNC has already solved the first problem. The usual metal nanoparticles, which facilitate 3 dimensional light matter interaction are made by nanoparticles capped with surfactants, and also in colloidal solutions. While the surfactants destroy the Raman intensity, the solution based synthesis are not stable beyond a few days rendering them unsuitable for device applications. NNC has already demonstrated nanoparticles of copper on silicon substrate. These nanoparticles are stable and remain intact as long as possible, which is a key bottleneck from solving the temporal stability.
4.4 Simulation of first order Raman spectra of nanoparticles

It has been discussed in previous reports that phonon confinement in nano-particles leads to a shift of the Raman peak, broadening of the spectra and asymmetric shape of the spectra. Asymmetric spectra means the spectra bends more towards the low wave numbers compared to the high wave numbers. The simulation of Raman spectra as per the RWL model was briefly discussed in previous report. This report shows the simulated data for nanoparticles of Silicon from 54nm, near bulk like to 3nm. Simulation was done using MATLAB and trapezoidal rule was used to perform numerical integration. A series of Raman spectra for these nanoparticles are shown from figure 4(a) till 4(m). Observe from these graphs for large particle size, the spectra is more like bulk, with a peak at 521cm⁻¹ and FWHM=4.7. Drastic changes in the spectra are observed at about 8nm and below. Observe that for the smallest dots of 8nm, 6nm, 5nm, 3nm etc, the peak shifts, there is a marked broadening and also the spectra is asymmetric. Unlike the bulk, which is a symmetric lorentzian, the small particles spectra are broader at low wavenumber side compared to high wave numbers side. This arises due to the negative gradient of phonon dispersion of Silicon. Once the spectra was simulated, the peak shift, broadening and asymmetry was measured and plotted as in figure1,2 and3.
Figure 4 - 2 Raman spectra for 54.3nm particle diameter, bulk like behavior.
Figure 4-3  Raman spectra for 27.15nm particle diameter
Figure 4-4  Raman spectra for 21.7nm particle diameter
Figure 4-5 Raman spectra for 19.5nm particle diameter
Figure 4-6  Raman spectra for 15.2nm particle diameter
Figure 4-7  Raman spectra for 13.03nm particle diameter
Figure 4-8 Raman spectra for 6.54 nm particle diameter, bulk like behavior.
Figure 4-9: Raman spectra for 5.43 nm particle diameter, bulk like behavior.
Figure 4-10 Raman spectra for 3.2 nm particle diameter, bulk like behavior.
CHAPTER 5
CONCLUSION AND FUTURE WORK

The fabrication of porous silicon through pores of porous alumina has been studied for various anodisation parameters and their optical characterization has been studied using photoluminescence and Scanning Electron Microscopy. Porous silicon has been successfully fabricated through pores of anodic alumina synthesized using sulfuric acid as the electrolyte for various parameters, for oxalic acid and also for phosphoric acid. The optical characterization has been performed by using photoluminescence using a 407nm laser pointer as excitation source and HORIBA LABRAM HR800 for optical characterization. The excitation peak has been found in the transition region between visible-NIR typically peaking from 690-720nm. The FWHM is typically about 200nm. The samples are luminescent and orange-red color can be seen by the human eye. The time of anodisation phase in hydrofluoric acid, such that alumina dissolution is minimized has been found to be about 45 seconds for a electrolyte composition of 49%HF:Ehtanol:DI Water of 1:1:1. The porous silicon through porous alumina was also prepared for various dopant types n, p, p++ types. Two 300W bulbs were used to implement light assisted anodisation in n type silicon and luminescent samples were obtained. Porous silicon formation through porous alumina was also studied for p++ samples, degeneratively doped at a resistivity of 0.001-0.005 ohm cm. Their optical properties were also studied using photoluminescence. Further microscopic characterization was studied using JEOL 7500 microscope. Porous alumina templates we were first fabricated and then electropolished porous silicon was formed within the pores of porous alumina by using a current density of 100mA/cm². The samples so formed
were imaged using JEOL 7500 FESEM for top view and cross section. The top view showed the porous alumina with some deformations and etching due to electrochemical dissolution in Hydrofluoric acid. The cross section FESEM image showed three distinct layers, corresponding to the bulk silicon substrate at the bottom, followed by nanoporous silicon, and capped with porous alumina. The cross section also showed evidence of some additional pore widening and etching that electrochemical dissolution in alumina may have caused, nevertheless alumina survived. The electropolished porous silicon through porous alumina will be characterized using reflectance and transmittance measurement at collaborator laboratories for their application as antireflection coating in solar cells.

The formation of modulated pores in porous alumina using alternate cycles of hard and soft anodisation has been studied. The phenomena has been studied in thin films for the first time and regimes corresponding to hard and soft anodisation have been investigate. The oxide growth rate has been monitored using LABVIEW based data acquisition system, which enabled the capture of voltage-time graphs. By systematic study of hard and soft anodisation, acid concentration, applied voltage and time of anodisation have been chosen to match the cell size in mild and hard anodisation. The samples have been characterized by scanning electron microscopy and the pore modulations have been studied. The future work will be to further build up on the modulated structures and study their applications in various devices.

The simulations studied the process control for dependence of sputtering power, gas flow rate and length of aggregation region on cluster size of nanoparticle. The optical properties of nanoparticles have been modeled by simulating the Raman characterization
of metal and semiconductor nanoparticles. For metal nanoparticles, the SERS behavior has been studied for gold and silver nanoparticles. A device to optimize SERS behavior has been proposed. The Raman characterisation of silicon nanoparticles has been simulated and the broadening due to quantum confinement of phonons has been modeled for nanoparticles with sizes ranging from 54nm down to 3nm.
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VITA

Graduate College
University of Nevada, Las Vegas

Neelanjan Bhattacharya

Degrees:

Bachelor of Electrical Engineering, Mumbai University, India, 2001

Master of Science, Pennsylvania State University, U.S.A., 2005

Dissertation Title: Fabrication, Characterization and Simulation of Non-Lithographic Nanostructures and Their Potential Applications.

Dissertation Examination Committee:
Chairperson, Dr. Biswajit Das, Ph. D.
Committee Member, Dr. Yingtao Jiang, Ph.D.
Committee Member, Dr. Mei Yang, Ph.D.
Committee Member, Dr. Yoohwan Kim, Ph.D.
Graduate Faculty Representative, Dr. Pradip Bhowmik, Ph.D.