HIGH-THROUGHPUT PLASMA NANOMANUFACTURING AND ITS APPLICATIONS

BY

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DISSEVERATION

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ABSTRACT

Traditional top-down or bottom-up nanomanufacturing processes involve nanoscale pre-patterning, surface-area-sensitive assembly processes or extreme fabrication conditions; therefore, none of them meets the requirements of scalable and translational nanomanufacturing processes in one or more aspects, and thus they all lack industry compatibility. The challenges in nanomanufacturing prevent many nanotechnology innovations from translating into commercial applications.

This dissertation presents a low-cost, high-throughput plasma-based nanomanufacturing process, called simultaneous plasma enhanced reactive ion synthesis and etching (SPERISE), to address the technical challenges in mass producing nanoscale structures, components, and devices. This process incorporates and synchronizes top-down reactive ion etching and bottom-up reactive ion synthesis in a single-step nanomanufacturing scheme, allowing a unique lithography-less autonomous creation of one-dimensional nanostructures. As a platform nanomanufacturing technology, the SPERISE process leads to numerous applications, and readily translates many nanoscale devices, such as biosensors, optoelectronic devices, and nanoengineered surfaces, into industrial mass production.

To pick a few of these applications, in this dissertation, I demonstrated a high-efficiency black silicon solar cell with nanotextured non-reflective surface, which significantly improved the light-trapping effect of conventional microtextured solar cells by wet chemical processes. Based on the SPERISE nanomanufacturing, a nanostructured plasmonic surface was also created cost-effectively, which exhibits unique physical and chemical properties, such as super light absorption, metal-enhancement fluorescence, surface-enhanced Raman scattering, and
superhydrophobicity and “coffee ring” elimination. Furthermore, a plasmonic nanoarray was fabricated with SPERISE process and incorporated in an electrically-stimulated biological microfluidic system to create an electro-optofluidic biosensor for protein kinase sensing and profiling and atomic level nano-bio interface studies. Last, the wafer-scale nanotip array fabricated by the SPERISE process was used as an electrochemical transfer printing mold to enable cost-effective, high-fidelity, high-resolution, and high-throughput printing of 3D metallic nanopatterns, which significantly improved the feasibility of tip-based nanomanufacturing as a next-generation nanolithography technology.
To my parents

Mr. Mingfang Chen and Ms. Jianmin Zeng

&

My dearest wife

Ms. Jingrui Lu

Without whom this achievement would not be possible.
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CHAPTER 1
INTRODUCTION

Long-term industrial and societal impact of semiconductor nanofabrication technology depends on its production rate, reliability, robustness, yield, cost, and the integration capability with micro- and macroscale systems. In recent years, various nanofabrication technologies have been developed for creating one-dimensional nanostructures on semiconductor substrates, including periodical or random 3D nanowires [1], nanopillars [2], and nanocone [3] arrays (Fig. 1.1). However, in despite of numerous successful demonstrations in nanoelectronics, nanophotonics, and nanobiotechnology, the commercial applications of these nanomaterials and nanodevices are very limited. The major obstacle is the incompatibility of existing nanomanufacturing techniques with industrial mass production. We believe that the advancement of nanomanufacturing innovation is the ultimate driver of nanotechnology commercialization and creating low-cost, high-throughput nanomanufacturing processes and equipment should be a main focus of the nanotechnology community in the next decade.
Figure 1.1: Summary of various forms of one-dimensional nanomaterials and their exemplary applications.

1.1 The challenges in nanomanufacturing

Like any existing industrial manufacturing processes, a scalable and translational nanomanufacturing process has to meet the following requirements:

- **Low Cost** – The nanomanufacturing process should be based on cheap and abundant materials, such as silicon, dielectrics. Any process involving excessive usage of noble metal or expensive materials is cost ineffective. Low energy consumption is another cost-relevant requirement.
• **High Volume** – The economy of scale requires a scalable parallel processing, which produces many devices in a batch. The continuous increase of wafer size (from 100 mm to 450 mm) in the semiconductor IC industry is a good example of high volume production. This requires a good spatial uniformity, low device-to-device variation, and low defect level.

• **High Throughput** – The process is able to produce many devices in limited time. The industrial manufacture of solar cells has a throughput of 2000 to 3000 wafer-per-hour. Intel fab plants have a throughput of around 100 wafer-per-hour. The manufacturing of “unconventional” biosensors or NEMS devices should not adapt any overlong nanomaterials growth process.

• **High Yield** – Repeatability is a key consideration in commercially viable nanomanufacturing process. High yield requires tight process control, reduction of processing steps, and inline monitoring and adaptive adjustment of manufacturing process. The inherently low yield techniques should be eliminated in nanodevice manufacturing.

• **High Controllability** – A full understanding of the mechanisms of a process and its controlling parameters is the prerequisite of high controllability. The nanomanufacturing process should be precisely tunable, and the results should be predictable by theoretical modelling and simulation. Also for the nanomaterials synthesized in solution or grown in furnace, the capability to handle, manipulate, and align the nanomaterials should be developed.

• **Low Environmental Impact** – The nanomanufacturing process should involve raw materials and processing gases/chemicals with low toxicity, and produce manageable amounts of waste. The toxicities of many nanomaterials are unknown; therefore, the
assessment of the potential environmental and health impact should be conducted before incorporating the nanomaterials into any commercial products.

Generally, existing nanomanufacturing techniques can be classified into either bottom-up or top-down processes. We will conduct a brief survey to assess the commercial potential of a few popular bottom-up and top-down processes based on the above metrics.

Bottom-up processes generally refer to growth techniques based on various phase transition mechanisms, such as Vapor-Solid (VS) [4], Vapor-Liquid-Solid (VLS) [5], and Solid-Liquid-Solid (SLS) [6]. VLS is the most investigated and implemented mechanism for the growth of one-dimensional nanostructures. Simply speaking, this process first adsorbs SiCl₄ vapor into Au-Si liquid alloy (under high temperature), and then the liquid alloy reaches a supersaturation at the liquid/solid interface leading to axial crystal growth (see Fig. 1.2a). In this process, the Au-Si liquid alloy serves as catalyst which rapidly adsorbs the SiCl₄ to the droplet to lower the activation energy of the normal vapor-solid growth. The gold nanoparticles (GNP) catalyst are created by an evaporation or sputtering process followed by a thermal annealing (at temperatures higher than the Au-Si eutectic point) process, or lithography with pre-defined shape and periodicity. This process requires the usage of noble metal, operates at high temperature, lacks controllability in orientation and surface roughness, and has a long processing time per batch. Therefore, although the VLS process serves as a cornerstone of nanowire research, it has not been adapted in industrial applications.

Molecular self-assembly (MSA) is another example of bottom-up nanomanufacturing (Fig. 1.2b). It refers to the spontaneous organization of molecules into structurally well-defined and stable arrangements through weak and noncovalent interactions. Such interactions include
hydrogen bonding, and ionic mediated hydrogen bonding. Short oligonucleotides, peptides, and lipid molecules are commonly used as building blocks to form biomaterials at nanometer scale. One unique feature of MSA nanomanufacturing is that it is a completely “green” manufacturing process and the nanomaterials it produces are bioabsorbable, biocompatible and biodegradable, which makes it very suitable for implantable medical applications. However, this technique is a self-guided process under strictly-controlled biological environments; therefore, it is prevented from deployment in volume production by its cost, scalability, and throughput.

DNA nanotechnology [7] is an emerging technique in recent years. It has benefited from the increase of computational power to precisely program complementary base pairs to form controlled two- and three-dimensional nanostructures at nanoscale. Figure 1.2c shows versatile 3D nanostructures, including signs, symbols, and alphabet, are created by this technique. These DNA “bricks” can be further assembled into large objects for either medical applications or to serve as templates to fabricate complex inorganic nanomaterials. However, the DNA nanotechnology, as a special case of molecular self-assembly, is again limited by its cost, scalability, and throughput. Although creating nanoscale objects was demonstrated, the competitive advantages of DNA nanotechnology over other nanomanufacturing methods at commercial level are very few.
Figure 1.2: Illustration of exemplary bottom-up nanomanufacturing techniques: (a) vapor-liquid-solid process, (b) molecular self-assembly, (c) DNA origami.

Top-down processes rely on nanoscale patterning with various nanolithography techniques, such as photo-, electron beam, nanosphere [3], nanoimprint [8], soft [9], and block copolymer [10] lithography, followed by an anisotropic plasma etching. Photolithography and e-beam lithography are widely adapted in industrial nanomanufacturing process, due to their versatility in creating nanopattens in arbitrary shapes and high controllability and repeatability. Other than photo- and e-beam lithography, nanoimprint lithography (NIL) probably is the most popular “unconventional” nanolithography method which has been semi-commercialized. It was first proposed by Stephen Chou at Princeton University in 1996 [11], and later added to the International Technology Roadmap for Semiconductors (ITRS) for the 32 and 22 nm nodes. The NIL is essentially a pattern transfer process which involves three steps: 1. Use a pre-created
nanopatterned template to mechanically deform the photosensitive or thermosensitive imprint resist (polymer). 2. Cure the imprint resist with heat or UV light. 3. Transfer the pattern to the underneath substrate by an anisotropic etching (usually RIE). It was demonstrated that the NIL can reach a sub-10 nm limit of resolution, which has a huge improvement over “conventional” lithography methods. An alternative electrochemical nanoimprint technique, called Superionic Solid State Stamping (S4), was developed by Nicholas Fang at MIT [12] in 2007. As shown in Fig. 1.3a, a pre-patterned superionic nano-mold is placed against a thin metallic film and an electric potential is applied between the mold and the film. The current causes the film to ionize and “dissolve” into the mold at the points of contact, and transfer the nanopattern to the uncontacted places.

Another very popular top-down nanofabrication method is nanosphere lithography (Fig. 1.3b). It uses self-assembled monolayers of polystyrene or silica nanospheres as lithography masks. People can either directly use the nanosphere assembly as etching masks and create high aspect ratio nanopillars (or nanocones) with reactive ion etching, or create nanoholes by using the nanosphere assembly as evaporation masks. This process can create nanostructures with precisely controlled spacing. However, the limitation is that it can only create periodic structures. In addition, the goodness of the self-assembled monolayers requires the strictly controlled evaporation process and the pre-treatment of the substrate surface; therefore, usually only a small area of closely-packed nanosphere film can be formed on a large substrate, and lots of point and line defects will form if applying this technique to full-wafer patterning. Furthermore, the synthesis of good quality nanospheres is also difficult, and monodisperse nanosphere solution with uniform diameter is expensive and unrecyclable.
Metal-assisted chemical etching (MacEtch) [13] essentially is not a nanolithography method, but an alternative anisotropic pattern transfer method than RIE process (Fig. 1.3c). It is a wet chemical based process relying on an electrochemical reaction at the interface between metal catalyst and semiconductor surface. It is generally accepted that the reduction of hydrogen peroxide takes place at the cathode, resulting in the injections of holes into substrates, and that the semiconductor substrate is dissolved at the anode through ionization process. The mechanism of the ionization is in dispute. Although many aspects of this reaction are still unknown, MacEtch is a very effective nanofabrication method, and the major advantage of MacEtch over RIE is its low-cost, batch-processing capability. However, MacEtch is dependent on many processing conditions, such as temperature of the solution, illumination, ratio of HF:H₂O₂, as well as the dopant concentration and crystallographic orientation of the substrate. Many of these mechanisms are not well understood. Also, the side-wall of the nanostructures after MacEtch tends to be porous and amorphous for unknown reasons. Due to the above uncertainties, the industrial applications of the MacEtch are very limited.
In conclusion, typical bottom-up and top-down nanomanufacturing processes involve nanoscale pre-patterning, surface-area-sensitive assembly processes or extreme fabrication conditions; therefore, none of them meets the requirements of scalable and translational nanomanufacturing processes in one or more aspects, and thus they all lack industry compatibility. The challenges in nanomanufacturing prevent many nanotechnology innovations from translating into commercial applications. This big gap between scientific demonstration and the commercialization of research outcomes calls innovative low-cost, high-throughput nanomanufacturing processes to push the limit of nanotechnology applications.

**Figure 1.3:** Illustration of exemplary top-down nanomanufacturing techniques: (a) superionic solid state stamping (S4), (b) nanosphere lithography, (c) metal-assisted chemical etching.
1.2 SPERISE as a low-cost, high-throughput nanomanufacturing process

In this dissertation, I introduce a unique, synchronized, and simultaneous top-down and bottom-up nanofabrication approach called simultaneous plasma enhanced reactive ion synthesis and etching (SPERISE). For the first time the atomic addition and subtraction of nanomaterials are concurrently observed and precisely controlled in a single-step process permitting ultrahigh-throughput, lithography-less, wafer-scale, and room-temperature nanomanufacturing. Rapid low-cost manufacturing of high-density, high-uniformity, light-trapping nanocone arrays was demonstrated on single crystalline and polycrystalline silicon wafers, as well as amorphous silicon thin films. The proposed nanofabrication mechanisms also provide a general guideline to designing new SPERISE methods for other solid-state materials besides silicon.

As a platform nanomanufacturing technology, SPERISE has many potential applications, including advanced materials, analytical chemistry, clean energy, nano-biotechnology, and optoelectronics. Figure 1.4 summarizes the applications that have been proposed and/or demonstrated in the past five years of my Ph.D. research. Some of the work has been completed and published, such as black silicon solar cells, fluorescence enhancement, surface-enhanced Raman spectroscopy, and kinase profiling nanoarray; some of the work is at the stage of proof-of-concept experimentation, such as hybrid solar cells, and colorimetric imaging. These research results will be properly arranged and presented in this dissertation with the outline below.
1.3 Outline of work

Chapter 2 introduces the cornerstone of my Ph.D. research, the simultaneous plasma enhanced reactive ion synthesis and etching (SPERISE) process, its mechanism, and the process control with various processing conditions. A dynamic study of the SPERISE process as well as microanalysis of nanostructured surfaces is also included. Chapter 3 discusses the application of
SPERISE process to fabricate antireflective black silicon solar wafers for photovoltaics applications. The fabrication and characterization of nanotextured black silicon solar cells was performed under both laboratory and industrial manufacturing conditions. Chapter 4 describes the application of SPERISE process in the fabrication of super-black metallic nanosurfaces with unique physical and chemical properties, such as antireflectivity, metal-enhanced fluorescence, surface-enhanced Raman spectroscopy, superhydrophobicity and eliminating “coffee ring” effect. The optical and plasmonic properties of the metallic nanosurfaces will also be theoretically studied with various computational electromagnetics methods. Chapter 5 discusses the protein kinase sensing and profiling using the nanoplasmmonic nanoarray and the electrically-amplified surface-enhanced Raman spectroscopy. An investigation of the nano-bio interfaces is also conducted by employing molecular dynamics (MD) method as a computational microscope at atomic scale. Chapter 6 uses the wafer-scale nanotip array fabricated by the SPERISE process as a nanoscopic printing mold for a highly-parallel tip-based additive electrochemical 3D printing. A nanotip-to-nanoparticle transfer printing has been demonstrated with one-to-one fidelity and 10-nm resolution. The nanoscopic surface topology and electrochemical dynamics of this nanomanufacturing process have been carefully investigated.

1.4 References


CHAPTER 2
SIMULTANEOUS PLASMA ENHANCED REACTIVE ION SYNTHESIS AND
ETCHING (SPERISE) NANOMANUFACTURING

2.1 Nanomanufacturing process and mechanism

The key mechanism underlying the SPERISE method is the concurrent reactive ion
c nucleation process with the reactive ion etching process. In a plasma-enhanced multiple ion
reaction system, the nanoscale gas-to-solid phase transition synchronizes with the nanoscale
solid-to-gas phase transition, which results in pseudo-uniform, complex, oxide nanoparticle
arrays gradually grown over the entire surface of silicon wafers. These arrays act as the etch
mask for the simultaneous anisotropic silicon etching. The SPERISE nanofabrication process is
shown in Fig. 2.1. Bare silicon substrates are prepared with a standard process and cleaned with
a wet etching process to remove the native oxide layer on the surface. In a reactive ion etcher
chamber, a silicon nanocone array is formed on the entire substrate surface via the single-step
SPERISE process with a reactive ion mixture of hydrogen bromide (HBr) and oxygen (O₂).
Bromine ions are the primary etching plasma to react with silicon atoms from the top surface
layer gradually to inside layers, while oxygen ions, bromine ions and silicon ions combined
together make up the building blocks to synthesize the complex silicon oxybromide compound
on top of the substrate surface layer. The simultaneous bottom-up and top-down reactions can be
summarized in several chemical reaction formulas (Eq. 1.1) by including the silicon oxidation.

\[
\begin{align*}
Si + 4Br^- \xrightarrow{\text{Etching}} & \text{SiBr}_4 \\
SiBr_4 + O^+ \xrightarrow{\text{Synthesis}} & \text{SiBr}_x\text{O}_y \\
Si + 2O^+ \xrightarrow{\text{oxidation}} & \text{SiO}_2
\end{align*}
\]

(1.1)
Figure 2.1: Schematic process flow of SPERISE nanomanufacturing.

Initially, randomly distributed seed points will be nucleated when bromine ions and oxygen ions simultaneously meet at some exposed silicon crystal lattice points on the surface (Fig. 2.2i) [1]. Within several seconds, the seed points will quickly grow into nanodots through a gas-to-solid nucleation process. These nanodots are less than 10 nm in diameter indicated by the corresponding scanning electron microscopy (SEM) images (Fig. 2.2i). What occurs at this stage is primarily a bottom-up process, creating the protective nanoscale mask array for both the subsequent nucleation and etching processes. The nanodots will keep growing over time around the initial nucleation point into larger hemispherical nanoparticles (Fig. 2.2ii). Simultaneously with the above nucleation process, exposed silicon surface is continuously etched by bromine ions. Because HBr has a very high reaction selectivity of silicon to silicon oxide (200:1), the growing silicon oxybromide (SiBr\textsubscript{x}O\textsubscript{y}) nanoparticle array acts as a constantly growing etch mask that protects the covered silicon surface. Consequently, the longitudinal nanostructures will be created by this self-controlled anisotropic etching process. As shown in the SEM image (Fig. 2.2ii), the bottom structures are nanocones with smooth sidewalls and the top structures are nano-hemispheres. The nanodots eventually grow into nano-hemispheres because the reactive ion flux is highly directional from the top, so the nucleation will preferably happen on the top of the nanodots. A similar nanoscale process was observed before [2]; however, the mechanisms controlling this process were not explored. As the etching of the nanocones continues, oxide
nucleation nanodots are also formed on the sidewall of newly exposed silicon nanocone surface besides the further growth of the nano-hemispheres on the top of the nanocones (see Fig. 2.2iii). A nano-mushroom structure can be seen with the sidewall covered by a layer of oxide nanodots (SEM image in Fig. 2.2iii). The SEM image also shows that the size and density of the nanodots synthesized on the sidewall gradually decrease from the top to the bottom part of the nanocones and there are no nanodots on the bottom of the sidewall at all. The size difference of the sidewall nanodots at different heights directly reflects the different time spent in the localized reactive ion synthesis process. This observation strongly supports the plasma enhanced oxide nanodots nucleation mechanism.
Figure 2.2: Schematic drawing of the three typical stages in the SPERISE process. Bromine and oxygen reactive ions interact with silicon to form synthesized oxide hemisphere and dots (orange) and etched silicon cone structure (green). Both illustration and corresponding SEM images at (i) 0–15 s, (ii) 15 s–2 min, and (iii) 2–5 min in the SPERISE process manifest this unique nanomanufacturing method.

2.2 The crystallographic dependence of the SPERISE reaction

In the scanning electron microscopy study, we found the nanostructures created on the three kinds of substrates after the same SPERISE process are quite different, which are
nanocones, nanopillars, and nanofrustums for the monocrystalline (Fig. 2.3a, d, g, j), polycrystalline (Fig. 2.3b, e, h, k), and amorphous (Fig. 2.3c, f, i, l) silicon substrates, respectively. The monocrystalline nanocones (Fig. 2.3a, d) have very sharp tips covered by oxide nano-hemispheres; the polycrystalline nanopillars (Fig. 2.3b, e) are high aspect ratio structures with identical top and base diameters; and the amorphous nanofrustums (Fig. 2.3c, f) are low aspect ratio structures with base diameter slightly larger than top diameter. However, after the oxide removal, all three nanostructures became nanocones with sharp tips and smooth surface profiles (Fig. 2.3g, h, i), which indicates that the polycrystalline nanopillars and the amorphous nanorods have a relatively thick layer of oxide covered on the surface of the sidewalls. In addition, there is a noticeable height reduction from the original nanopillars/nanorods to the nanocones after oxide removal, which is primarily due to the removal of the nano-hemispheres on the top of the nanocones. In the cross-sectional views of the three nanocones (Fig. 2.3j, k, l), the height, base diameter and the aspect ratio differences manifest more clearly. These differences are consistently observed in all of our experiments. We believe that the geometric differences of the nanostructures based on the three different crystallographic substrates imply an inherent mechanism in the SPERISE process. It is crucial to explore this mechanism for better understanding as a guideline for controllable and deterministic nanofabrication.
Figure 2.3: SEM images of nanostructures created by SPERISE process. (a–f) Nanostructure profiles on (a,d) single crystalline, (b,e) polycrystalline, and (c,f) amorphous silicon substrates before oxide removal. Nanocones, nanopillars, and nanorods are created on these three substrates, respectively, with clearly visible oxide nanohemispheres on top. (g–l), Nanostructure profiles on (g,j) single crystalline, (h,k) polycrystalline, and (i,l) amorphous silicon substrates after oxide removal. All three substrates become nanocones with extremely smooth sidewall and sharp tips. The nanocones showed different aspect ratios, with the sharpest nanocones on polycrystalline substrate and the most obtuse nanocones on amorphous substrate, which suggests the crystalline structure of the substrates impacts the nanocone profiles.
2.3 Density and height control of nanocone array

The simplicity and robustness of the SPERISE nanomanufacturing mechanism ensure the extremely high repeatability of the process and controllability of the nanostructures. Once a recipe is obtained for a reactive ion etcher, it can repeatedly produce the structures with the same density, height, and aspect ratio. In contrast, the nanostructures with different morphologies can be predictably produced by tuning the fabrication conditions with the guidelines stated in section 2.2.

The density controllability is demonstrated by a series of control experiments with respect to the mixture ratio of HBr and O₂. In our experiments, the time was fixed to 3 minutes, the flow rate of HBr was fixed at 20 sccm, and the flow rate of oxygen O₂ was tuned from 0.8 sccm to 1.3 sccm by 0.1 sccm. Other conditions were kept the same in all experiments. The results of the control experiments are shown as Fig. 2.4, in which a clear density increase can be seen. The counted average numbers are 5, 11, 17, 23, 28 nanocones / µm² from Fig. 2.4a to Fig. 2.4e, and the nanocones joined into each other under 1.3 sccm oxygen flow rate.
Figure 2.4: Nanocone array density control with polycrystalline silicon substrates. The mixture ratios of hydrogen bromide (HBr) and oxygen (O2) were (a) 200:8, (b) 200:9, (c) 200:10, (d) 200:11, (e) 200:12, (f) 200:13, respectively, with other fabrication conditions the same. The average densities of nanocone array were measured under scanning electron microscope (SEM).

The height controllability is demonstrated by a series of control experiments with the varying fabrication times. As an example, four identical amorphous silicon substrates with the fabrication time 5, 10, 20, and 40 seconds under the same conditions were scanned with an atomic force microscope (AFM). The surface morphology of the a-Si substrates is shown in Fig. 2.5, and the pseudo-color intensity represents the relative height of the structures. One fact that has to be noted is that the a-Si nanocone array is so dense that possibly the AFM tip could not reach the bottom of the 40-seconds (even 30-seconds) device, and the surface morphology shown here is the oxide nano-hemispheres and the valleys between the nanocones. In spite of the limitation of the instrument, the measured height range gives us an approximate relationship between the height and the corresponding fabrication time, i.e. 9.5 nm, 28.0 nm, 50.6 nm, and >93.8nm for the 5s, 10s, 20s, and 40s substrates, respectively.
Figure 2.5: Nanocone array height control on amorphous silicon substrates. The average heights of the nanocone arrays were measured with atomic force microscope (AFM) for the a-Si substrates processed by SPERISE for (a) 5 seconds, (b) 10 seconds, (c) 20 seconds, and (d) 40 seconds, respectively, with all other fabrication conditions the same.

2.4 Micro-nano hierarchical structures

In addition to the independence of crystalline orientations, the SPERISE process is also independent of the topological structures of the original surfaces, and able to create nanocones on top of various 3-dimentional microstructures.

We first performed nanotexturing on wet chemical textured micropyramid structures. Figure 2.6a shows the atomically smooth pyramid surface after the KOH anisotropic etch. Figure 2.6b shows the nanomask formed on the micropyramid at the initial texturing process. If
looking carefully, a layer of sub-10 nm nanodots can be seen uniformly distributed on the surface, which confirmed the mechanism of the SPERISE process. After 1.5 min, the pyramids became grassy as shown in Fig. 2.6c, and if we zoom into the grassy surface and look at the cross section, we can easily tell that the grass layer was high density nanocones around 150 nm in height (Fig. 2.6d). The visual appearance of the micro-nano hierarchical structures was blacker than the original micropyramid structures.

**Figure 2.6:** Nanotexturing on top of micropyramid structures created by standard anisotropic wet texturing. (a) Original micropyramid surface. (b) Nanomask formed on the micropyramid. (c) Grass micropyramid created by successful nanotexturing. (d) Cross section of micro-nano hierarchical structures. The dashed line indicates the interface between nanocones to the bulk silicon.

We further applied the nanocones to inverted micropyramid structures. The inverted pyramid was first created by photolithography followed by KOH anisotropic etch. The etching
Process automatically stops upon the formation of pyramids. The window size of each pit was 1 µm × 1 µm. As shown in Fig. 2.7, the grass-like nanocones were uniformly formed on the entire surface, including the slanted micropits and the planar surface between the pits.

**Figure 2.7**: Nanocone texture created on inverted micropyramid array. The inset in (a) is the original inverted pyramidal surface. The inset in (b) is the side-by-side comparison of untextured and textured samples. The nanotextures were on both smooth surface and microstructured area. The scale bars in (a) and (b) are 2 µm and 1 µm, respectively.

The above experiments show that the Omni Black process applies to any 3D surface topology and is independent of crystalline orientations, which demonstrates the versatility of the SPERISE nanomanufacturing process.

### 2.5 Dynamics of SPERISE reaction

In an effort to understand this mechanism as a guideline for controllable and deterministic nanofabrication, we carried out a systematic morphological measurement and comparative analysis of the nanostructures for three kinds of silicon substrates under a typical nanofabrication condition (see Fig. 2.8a-f). **Figure 2.8a** shows the average heights of nanostructures before (solid lines) and after (dashed lines) the oxide removal. All these data indicate that the height, \( h \), of the nanostructures before and after oxide removal maintains the...
relationship $h_{sc-Si} < h_{pc-Si} < h_{a-Si}$, and the total height reduction (dash-dot lines) is also in an order $h_{sc-Si} < h_{pc-Si} < h_{a-Si}$. As the height reduction is primarily due to the removal of the synthesized nano-hemispheres on top of nanocones, this result implicates the nucleation rate of sc-Si < pc-Si < a-Si, which is consistent with the measured diameter of synthesized nano-hemispheres in Fig. 2.8b. As can be seen from the plots, a nano-hemisphere of a-Si material grows much faster than one of pc-Si and sc-Si, and a nano-hemisphere of pc-Si grows slightly faster than one of sc-Si. Also, we found that the height difference before and after oxide removal (dash-dot lines in Fig. 2.8a) is much larger than the radius of the nano-hemisphere. This discrepancy is consistently observed in all experiments; hence it cannot be explained as an error in the measurements. It implicates a unique inherent mechanism in the SPERISE process. The height discrepancy is calculated in Fig. 2.8d, in which a nonlinear monotonic increase is shown. Furthermore, the base diameter is measured in Fig. 2.8e, in which it increased linearly with rates 35.03 nm/min, 22.32 nm/min, and 58.60 nm/min for sc-Si, pc-Si, and a-Si, respectively. The aspect ratio is plotted in Fig. 2.8f by dividing the measured height after oxide removal by the base diameter. It is very consistent with different processing times, with around 3:1, 5:1, and 2:1 for sc-Si, pc-Si, a-Si nanocones, respectively. This data demonstrates the high repeatability and controllability of the SPERISE process.
Figure 2.8: (a) Average height measurements of the nanostructures on sc-Si, pc-Si, and a-Si before and after the oxide removal, as well as total height reduction caused by oxide removal. (b) Average diameter of the oxide nanohemisphere. (c) Average nanocone height below nanohemisphere cap. (d) Average height of complete inward-oxidized region. (e) Average nanocone base diameter. (f) Aspect ratio calculated from the measured average height and base diameter after oxide removal. The inset images represent the corresponding geometries of the plotted data. From a–f, the best fit curves of each data group are also plotted.
2.6 The underlying mechanisms of the SPERISE reaction

On the basis of the above findings, we propose that the sidewall oxide formation was concurrently governed by two different physical and chemical processes (Fig. 2.9a). One process is the bromine and oxygen ion associated nucleation on the newly etched silicon surface, which shares the same mechanism with the nano-hemisphere synthesis (purple region in Fig. 2.9a). The other process is the inward oxidation in which the oxygen and bromine ions penetrate the nucleated oxide layer and associate with the sidewall silicon crystal lattices to form oxide inwards from the original etched sidewall (yellow region in Fig. 2.9a).
Figure 2.9: Nanocone profile formation mechanism and characterization for single crystalline (sc-Si), polycrystalline (pc-Si), and amorphous (a-Si) substrates. (a) Schematic of nanostructure profile formation mechanism. The orange half-circle on top represents the synthesized oxide nanohemispheres. The purple, gold, and olive green regions represent the oxide layer created by outward reactive ion nucleation, the oxide layer created by inward penetrated ion oxidation, and the actual nanocone profiles after oxide removal, respectively. (b) TEM image shows core–shell structure of pc-Si nanopillar before oxide removal. The core is the silicon nanocone, and the shell is the oxide layer formed primarily by outward reactive ion nucleation. (c) High resolution SEM image showing the neck region of sc-Si “nanomushrooms”. A core–shell structure under the oxide nanohemisphere cap indicates the complete oxidation of the original silicon nanotip, which is primarily caused by inward penetrated ion oxidation.

In the first process, the oxide layer grows outward from the original sidewall. The rate of the nucleation process for both sidewall oxide layer and nanohemisphere is directly related to the
etch rate of silicon materials because quicker etching produces higher localized silicon ion concentration near the silicon nanocones surface, hence the possibility of nucleation events is increased. As shown by the solid lines in Fig. 2.8c, the etch rate of the three types of silicon materials is on the order of sc-Si < pc-Si < a-Si, with 112.2 nm/min, 115.9 nm/min, and 121.7 nm/min for sc-Si, pc-Si, a-Si nanocones, respectively. Consequently, the growth of the diameter of nano-hemispheres (Fig. 2.8b) is also on the same order. Furthermore, the sidewall profile differences between the sc-Si nanocones, pc-Si nanopillars, and a-Si nanorods shown in Fig. 2.3a, b, c, can be also explained with this mechanism, by which the sidewall oxide thickness maintains the same order as the etch rate (sc-Si < pc-Si < a-Si). Meanwhile, the sidewall profile is also determined by the difficulties of the reactive ions associating with the sidewall surfaces. The outward nucleation process occurs once the new sidewall silicon surface is exposed. For sc-Si, the reactive ions are preferably associated with exposed and less stable crystal lattice points; therefore, nucleation only occurs at pseudo-random locations and forms oxide spots on the sidewalls at low rates (see Fig. 2.2b-iii, Fig. 2.3a, d and Fig. 2.9c). Only a thin layer of oxide is formed on the sidewalls and the overall structure profile remains nanocones for sc-Si. For pc-Si, the reactive ions are preferably associated with exposed grain boundaries [3] as well as the exposed crystal lattice points on each crystalline patch; hence, the nucleation process happens nearly everywhere on the sidewall and a nearly uniform oxide layer forms on the sidewall at higher nucleation rates (see Fig. 2.3b, e and Fig. 2.9b). The nucleation time difference causes a thicker and thinner oxide layer at the top and bottom, respectively; consequently, the overall profile looks like nanopillars for pc-Si. In the case of a-Si, ion association happens everywhere on the sidewall. The nucleation rate is the highest, so a much thicker and uniform oxide layer was formed (see Fig. 2.3c, f) and the top oxide nano-hemispheres for a-Si samples are much
larger than those for sc-Si and pc-Si samples (see Fig. 2.3a, b, c). The hemispherical caps with protruded rims on the pc-Si nanopillar in the SEM image of Fig. 2.9b clearly separate the bottom-up synthesized structure and top-on etched structure, which supports the plasma assisted nucleation mechanism.

The second process is similar to the thermal oxidation, in which the oxidation happens by inward movement of oxidants rather than by outward movement of silicon [4]. The difference, however, is that in thermal oxidation, the oxidant moves by the diffusion along molecular density gradient. In this process, the oxidant moves by physical bombardment. The thickness of the inward oxidation layer is determined by the thickness of the outward nucleation layer; the thicker the outward nucleation layer, the harder it is for ions to penetrate it. As shown in Fig. 2.8d, the thickness is sc-Si > pc-Si > a-Si, which is in the reversed order of the nucleation process in Fig. 2.8b. Although the thickness of this oxide layer is minor compared with the outward nucleated oxide, this physical process is critical in explaining the discrepancy of the total height reduction by oxide removal (dash-dot lines in Fig. 2.8a) and the radius of the nanohemisphere (Fig. 2.8b).

The core-shell structure with crystalline core and amorphous shell visualized on the sidewall of the nanopillar from the high resolution TEM image of Fig. 2.9b supports the aforementioned outward nucleation and inward oxidation mechanisms. Clear core-shell structures with darker silicon crystal core and brighter oxide shell are also observed near the neck region of the sc-Si nano-mushroom shown in Fig. 2.9c. There is a pure oxide region (brighter) between the silicon nanotip (darker) and the oxide nano-mushroom cap, which indicates that the region just beneath the mushroom cap has been completely oxidized in the inward oxidation process.
Besides the morphological determination by the aforementioned two processes, because the nano-hemispheres act as the etching mask of the silicon, the aspect ratio of the originally etched nanocone profile is determined by the lateral growth rate of the oxide nano-hemispheres. The etch directionality is also influenced by the crystallographic orientation of the substrates to some extent due to higher etch rate along the <100> plane than the <111> plane.

2.7 Characterization of black silicon materials

Figure 2.10a shows a transmission electron microscopy (TEM) image of the fabricated nanocone structure. The diameter of the cone at the base is about 180 nm and the height varies between 300 and 400 nm. TEM investigation (Fig. 2.10b) revealed that the crystal structures of the cones are free of dislocations and two-dimensional defects (only point defects are expected due to bombardment of low energy ions in RIE process). The inset shows a selective area electron diffraction (SAED) pattern of the nanocone. Figure 2.10b also shows the sub-10-nm tip structure of the nanocone.
Figure 2.10: (a) TEM showing the detailed structure of a single nanocone of the black Si. (b) High resolution TEM of the nanocone structure and the inset showing a SAED pattern of the nanocone.

We obtained the PL spectra by illuminating the sample with a 442 nm laser source and measuring the luminescence from 500 to 800 nm at room temperature. Figure 2.11a shows the PL spectrum from the sample with an integration time of 300 s. After the deconvolution of the peaks and Gaussian curve fitting, the PL spectrum contains three peaks at 1.73 (718 nm), 1.86 (667 nm), and 1.95 eV (637 nm), respectively. At low temperature (77 K), the peak at 650 nm gets enhanced as compared to peak at 515 nm (Fig. 2.11b). The green band (~510-580 nm) is generally attributed to the recombination of carriers at oxygen-related defect centers (“defects related PL”) [5]-[10], and the red band (~635-720 nm) is due to recombination of confined excitons in Si nanocluster (“confinement related PL”) [5], [8], [11], [12]. Figure 2.11b shows an increase in intensity for band at 650 nm at low temperature. This can be explained by the quantum confinement of the excited carriers at the tips of the nanocone [8]. At low temperatures,
excited carriers are localized at these weak potential wells or traps formed by the defects. At lower temperature, there is reduced probability of non-radiative recombination through defect centers and increased zero phonon recombination probability for electron-hole pair. Hence, the intensity of PL at lower temperature (77 K) is higher than PL at room temperature (300 K). Figure 2.11b shows that the peak wavelength of the green luminescence band remains unchanged after lowering the temperature, although there is slight increase in intensity. This provides further evidence that the green luminescence band is defect-related PL. Furthermore, with the increase in temperature, the carriers are thermally excited and move to deeper potential wells close to band edges. As shown in Fig. 2.11c, the band-edge PL intensity is higher than the confinement related PL intensity. Since our system uses a Si based detector, we are unable to see the whole band-edge spectrum for Si. Figure 2.11d shows PL spectra for black Si with different excitation energies. We observe a consistent red shift of PL peak with decreasing the excitation energy from 2.8 to 2.33 eV (442-532 nm). The red shift of the PL peak is an indication of defects related PL [13].
Figure 2.11: (a) PL spectrum from black Si with excitation laser of 442 nm. (b) PL at 77 K and 300 K using excitation wavelength of 442 nm. The integration time is 300 s. (c) Visible and band-edge PL spectra using excitation wavelength 532 nm. (d) Comparison of PL spectra using excitation wavelength of 442, 488, and 532 nm.

**Figure 2.12a** shows the cathodoluminescence (CL) spectrum for black Si with an excitation probe current of 25 nA. The measured CL spectra are deconvoluted and fitted to a Gaussian shape. Mainly three Gaussian bands are observed: green, red, and infrared. The green CL band (565 nm or 2.2 eV) is attributed to point defects related to oxygen deficit (Si–Si bond) [14]. The observed red band (650–670 nm or 1.9-1.85 eV) is generally assigned to nonbridging oxygen hole centers in oxygen deficient SiO₂ environment [15] or recombination via Si-nanocrystal-SiO₂ interface defects [16, 17]. The band at 750 nm (1.65 eV) may also originate from a nonbridging oxygen hole center mostly at Si-SiO₂ interface [18]. The infrared
band (1.4-1.6 eV) is attributed to band-band transition in Si-nanocluster [14]. Figure 2.12b shows the variation of CL spectrum with increasing the probe current. The intensity of the CL spectra increases with increase in the probe current. The earlier observed PL peak at 667 nm is also observed in all CL spectra (Fig. 2.12b). The secondary electron image (SEI) and panchromatic CL (panCL) image of the black Si over a 4 μm × 2.67 μm area are shown in Figs. 2.12c and 2.12d, respectively. The bright spots are due to the presence of oxide layers on the black Si surface. The luminescence from black Si can be clearly seen from the panCL image.

**Figure 2.12**: (a) Grating corrected CL spectrum of black Si using probe current of 25 nA. (b) Comparison of CL spectra with increasing the probe current. (c) SEI of the black Si. (d) Panchromatic CL image of the same region shown by SEI.
In conclusion, we observe photoluminescence and cathodoluminescence from crystalline black silicon without additional thermal treatment. The PL and CL study shows three bands: the green band is associated with point defects, the red band is related to the surface and interface defects, and the infrared band can be attributed to the electronic transition between quantum confinement induced widened band gap in the vicinity of the sub-10 nm nanocone tip. Our results indicate the potential applications of the sharp-tip nanocone black silicon structures in active silicon photonic devices.

2.8 References


CHAPTER 3
BLACK SILICON SOLAR CELL

3.1 Introduction

The greatest challenge facing the solar industry is its high cost per kilowatt hour. The cost of solar energy is the highest among all the renewable energy sources, which makes solar, the most abundant of renewable energy sources, become the smallest sector in global energy consumption. The rapid growth of global energy demand now trumps environmental safety and urges the cost reduction of solar power.

Fundamentally, cost reduction can be accomplished by increasing the energy output of solar cells and reducing manufacturing costs. To achieve this goal, countless technical strategies have been proposed, including using new materials and adopting new cell structure design. However, despite of all them, reducing surface reflection and enhancing light capture by texturing the front surface is the first step in all manufacturing processes and is extremely critical for all types of silicon solar cells.

Wet chemical texturing, either in an alkaline solution or in an acidic solution, is the most widely adopted method in industry manufacturing. Alkaline texturing has proven to be effective for monocrystalline silicon solar cells. However, it is dependent on crystalline orientation, so is ineffective for multicrystalline silicon solar cells. Hence, acidic texturing, as an isotropic etching method, was developed for multicrystalline silicon solar cells. However, this method relies on surface damage to initiate texturing process, so it is ill suited for all silicon wafers or thin films.
produced by kerfless wafering technologies. Therefore, there is no industrial approach completely effective for any silicon surface.

Additionally, conventional texturing has several significant drawbacks in terms of performance. First of all, it can only reduce surface reflectance to around 20%; even combining with antireflection coating the reflectance is still around 10%. It is also ineffective for blue and infrared light, limiting the peak efficiency of solar cells. Secondly, the antireflection property is dependent on incident angle. Surface reflection increases rapidly with the increase of incident angle, which has notable negative impact for cell performance in the early morning and late afternoon.

Other challenges in texturing process include: 1. the silicon material loss introduced by texturing process could become more and more significant with the adoption of thinner and larger solar wafers. 2. Double-sided texturing is not compatible with most high efficiency cell concepts, such as industrial passivated emitter and rear cells (i-PERC). Innovative surface texturing technologies are critically needed in the technology roadmap.

SPERISE nanotexturing is a disruptive solution to solve all aforementioned problems, and simultaneously reduces the manufacturing cost and boosts the cell efficiency. A comparison of the surface structures created by conventional wet chemical texturing and SPERISE nanotexturing is shown in Fig. 3.1. The conventional ones have micropyramids with random sizes ranging from 5 – 10 µm on each side of solar wafers. In contrast, the nanotextured ones have nanocones with consistent sizes around 500 nm on a single side. The structural differences determine the effectiveness of anti-reflection and light trapping, the amount of wasted silicon
materials in the manufacturing process, and the goodness of process control and product uniformity.

**Figure 3.1**: Standard solar cell manufacturing process and a side-by-side comparison of conventional texturing and SPERISE nanotexturing.

### 3.2 Antireflection properties of nanotextured mono- and multi-crystalline wafers

**Figure 3.2a, b**: show the measured hemispherical reflectance from 300 nm to 1100 nm of the wafer scale single crystalline and multicrystalline silicon nanocone substrates, as well as corresponding types of silicon substrates with conventional alkaline or acidic texturing, and commercial solar cells with conventional alkaline or acidic texturing and Si$_x$N$_y$ antireflection coating. Light is from normal incidence in this measurement. Remarkably, the sc-Si nanocone samples produced by SPERISE process have less than 2% reflection in the ultraviolet (UV), visible, and near infrared (NIR) light ranges (**Fig. 3.2a**) without any additional antireflective
coating. The samples exhibit better antireflection properties than not only sc-Si with alkaline texturing, sc-Si with alkaline texturing and Si$_x$N$_y$ antireflection coatings, but also other previously reported silicon nanotextured surfaces. Compared with multicrystalline silicon substrates with acidic texturing, multicrystalline silicon substrates with alkaline texturing and Si$_x$N$_y$ antireflection coatings, the multicrystalline silicon substrates with SPERISE nanotexturing have even greater antireflection properties. As shown in Fig. 3.2b, a conventional Si$_x$N$_y$ antireflection coating has especially low response for blue light (350 nm – 450 nm). In sharp contrast, the strong reflection peak in blue light region is completely eliminated for the mc-Si nanocone substrate with SPERISE nanotexturing. In addition, the reflectance in the entire visible light region is below 5%, and only increases to 10% after 1100 nm.

**Figure 3.2:** Antireflection property of SPERISE nanotextured (a) monocrystalline and (b) multicrystalline solar cells.
3.3 Optical absorption properties of nanotextured crystalline and amorphous silicon surfaces

To quantitatively characterize the optical absorption of the silicon nanocone array substrates, reflection and transmission spectroscopy measurements were carried out respectively. The normalized optical absorption is calculated by subtracting the sum of normalized reflection and transmission from unity. The total reflection and transmission from all angles were measured at the wavelengths ranging from 300nm to 1000nm. The optical reflectance at all angles in the hemispherical space was measured by Varian Cary 5G UV-VIS-NIR spectrophotometer with a Cary integrating sphere attachment. A reflectance standard sample (reflectance exceeding 99% from 400 nm – 1500 nm) was used to calibrate the system first, and the reflectance of the samples were measured at the wavelengths ranging from 300 nm to 1000 nm (the most reliable range of the equipment). The transmission in the same wavelength was measured by a standard setup of the system. This setup is only able to carry out the measurement with the normal incident angle.

An integrating sphere with a center mount sample holder stage (Labsphere RTC-060-SF) was used to characterize the relationship of absorption to angle of incidence (AOI) (Fig. 3.3). In our setup, the illumination was provided by a tungsten halogen light source. The beam was collimated and entered into the sphere through a small aperture. The light was simultaneously collected by an Ocean Optics broadband spectrometer (450 nm – 1000 nm) through the detector port of the sphere. The substrates were fixed by a center mount clip style sample holder, which can change the angle from 0° - 90° with the resolution of 1°.
Figure 3.3: Illustration of integrating sphere measurements [1]. (a) Configuration for transmission measurements. The incidence beam angle variation was achieved by the eucentric tilt of the entire sphere apparatus. (b) Configuration for reflection measurements. The incidence beam angle variation was achieved by rotation of the reflection stage within the sphere.

As can be seen from a typical absorption spectrum of a sc-Si nanocone substrate reflecting the relationship of absorbance to angle of incidence (AOI) and wavelength (Fig. 3.4), the absorption of the nanocone substrate is around 99% in the visible light range at all AOI from 0° - 50° and slightly drops below 90% beyond 1000 nm. The reason for the angle independence property is probably that the pseudo-random spatial arrangements of tightly packed nanocones eliminated the anisotropic angular absorption inevitably caused by perfect periodic structures [1]. The angle independence makes the nanocone substrates better omnidirectional anti-reflectors than regular nanoarray substrates.
Figure 3.4: Angle independent absorption of the single crystalline silicon nanocone array. The measurements were done with the incident light from $0^\circ$ to $50^\circ$.

Figure 3.5a shows the optical absorption measurement for a uniformly deposited a-Si thin film on glass substrate and an a-Si thin film substrate with SPERISE nanotexturing with wavelength from 300 nm to 800 nm. Compared with a uniform, thin film a-Si deposited on glass, the absorption enhancement of the a-Si nanocone structures in the visible light region is remarkable; the absorption is nearly 100% in the blue and near UV light regions at a-Si bandgap of $\sim1.7$ eV. These and other data indicate the nanocone array may have an average absorption of least about 95% of incident light having a wavelength of between about 300 nm and about 500 nm. The absorption also increases with processing time as shown by the color change over time (Fig. 3.5b), indicating the taller the nanostructures the better the light-trapping.
3.4 Theoretical simulation of light absorption

Two theoretical simulations were performed to support the light trapping effect of the nanocone array fabricated by the proposed SPERISE mechanism. The nanocone in our simulations is 500nm in height and 200nm in width with single crystalline silicon (sc-Si) material.

The quantitative light absorption simulation is based on the effective medium theory [2], in which the geometry of the nanocones is approximated by an effective reflective index calculated by the relative fractions of silicon and air. An unpolarized planar wave was generated from the normal incidence, and the reflective wave was collected at the same position. The simulation result shows the nearly total absorption in ultraviolet, visible and near infrared wavelength range by sc-Si nanocone arrays, while the original bare sc-Si surface has much lower light absorption especially for blue light (Fig. 3.6a). The excellent light trapping effect could be due to a nearly perfect impedance matching between bulk silicon and air provided by the
nanocone layer through a gradual reduction of the effective refractive index away from the surface [3].

The spatial distribution of electric field and energy flow is simulated by a finite element electromagnetic analysis of a two dimensional periodic silicon nanocone array. The actual nanocone array is randomized and it has no surface resonance mode as in the perfect periodic arrays such as surface photonic crystals, so the absorption of randomized nanocone array extends to broader wavelength range. As shown in Fig. 3.6b, the vast majority of light was guided by the silicon nanocone arrays into the silicon material rather than being reflected back.

**Figure 3.6:** Theoretical simulation of the light absorption by the single crystalline silicon nanocone array. (a) The optical absorption of single crystalline silicon nanocone array compared with bare single crystalline silicon substrate. (b) Light trapping effect of the silicon nanocone array. The geometry of the nanocones in this simulation is 500nm in height and 250nm in width. The demonstrated result is of the incident light of 700nm wavelength. The surface color, representing the intensity of the Z component of the electric field, is defined by the color map on the right side. The result shows that most of electromagnetic wave illuminated from the top is guided by the nanocone structures and penetrates deep into the underneath material, while the reflected field at the top is nearly zero.
3.5 Black silicon solar cell – laboratory fabrication

As shown above, the silicon nanocone array created by the SPERISE process has remarkable omnidirectional light absorption enhancement. To demonstrate the photovoltaic application of this nanomanufacturing method, a batch of single p-n junction solar cells was fabricated by the process shown by the schematic Fig. 3.7a. Firstly, a high density nanomushroom array was formed on highly doped (0.001 – 0.005 $\Omega \cdot$cm) p-type monocrystalline silicon wafer (University Wafer) by the SPERISE process as discussed before. The substrate then went through the HF oxide removal and HNO$_3$:HF (50:1) surface damage removal processes. The p-n junction was formed by spin-on phosphorus doping processes (P509 Dopant from Filmtronics), and a radial junction with junction depth around 200nm was formed at 950°C for 10 minutes. Phosphorus glass etching is performed afterwards. ITO and Au sputtering followed by a rapid thermal annealing (RTA) at 400°C led to a conformal front and back contact respectively covering the whole surface. The ITO conformal top contact has two advantages: (i) compared with conventional finger grid top contact, it shortens the travel distance of charge carriers, significantly reducing the series resistance; (ii) it reduces surface recombination by eliminating the dangling bonds on Si surface. Finally, edge isolation is achieved by mechanical sawing. Control planar silicon solar cell was fabricated with the same process from phosphorous doping step to edge isolation step. Even though only sc-Si wafer was used in this proof-of-concept study, the fabrication procedure demonstrated here should be transferable to pc-Si wafer and a-Si thin film solar cells.

Figure 3.7b, c show the I-V characteristics of exemplary nanocone black silicon and planar silicon control solar cells under AM 1.5G illumination. The average $J_{sc}$ of planar and
nanotextured sc-Si solar cells are 32.2 mA/cm$^2$ and 35.9 mA/cm$^2$ respectively. The increase of $J_{sc}$ directly comes from the enhanced photon energy captured by the surface nanostructures. Although the solar-weighted absorption of the sc-Si nanocone surface has around 20% enhancement over planar silicon surface, the $J_{sc}$ of the nanotextured sc-Si solar cell has only 11.5% enhancement over planar sc-Si control cell, which might be due to the larger surface area, and thus heavier surface recombination of the nanocone array solar cell. It indicates that surface recombination has a strong impact on the ultimate cell performance; thus, a better surface passivation technique needs to be considered in future work to maximize the light absorption gain by the nanostructures. The $V_{oc}$ for nanocone and planer solar cells are 631 mV and 610 mV respectively. $V_{oc}$ might be enhanced by more effective charge carrier collection through the radial junction. The fill factor of a nanocone solar cell is 0.80, which is slightly higher than 0.78 of planar solar cell. The efficiency of nanocone solar cell is 18.1%, which represents 18.3% enhancement over the 15.3% of a planar solar cell, and is better than the efficiency of similar nanotextured solar cells reported in the literature.
Figure 3.7: Nanocone array solar cell fabrication process and I-V characteristics. (a) Schematic nanocone array solar cell fabrication process. Nanomushroom array was first created on planar surface by SPERISE process, followed by the oxide removal and surface damage removal. Afterwards, a spin-on phosphorous doping was performed followed by a phosphorus glass etching to form a p-n junction. Then, a layer of ITO and Au were sputtered and then annealed to form conformal top and bottom contacts respectively. Lastly, edge isolation was completed by mechanical sawing. The planar control solar cell was fabricated with the steps ③ - ⑥. (b) I-V characteristics of planar control solar cell, which had $J_{sc} = 33.2$ mA/cm$^2$, $V_{oc} = 610$ mV, fill factor 0.78, and efficiency 15.3%. (c) I-V characteristics of nanocone array solar cell, which had $J_{sc} = 35.9$ mA/cm$^2$, $V_{oc} = 631$ mV, fill factor 0.80, and efficiency 18.1%.
3.6 Black silicon solar cell – industrial manufacturing

To further demonstrate the technical advantages of SPERISE nanotexturing, we sent nanotextured full-size mono- and multicrystalline wafers (156 mm × 156 mm) to PV manufacturers for cell processing and testing. The cells were produced by an industrial standard full aluminum back surface field process. A comparison was made between conventionally-textured cells and nanotextured cells. Figure 3.8 shows both color and texture difference of two exemplary multicrystalline cells. The crystal grains were clearly seen on top of conventionally isotextured cells. In contrast, as the SPERISE process was independent of crystalline orientation, the crystal grains were no longer visible by naked eyes for nanotextured cells. With overall reflection lower than 5%, the highly uniform black color of multicrystalline cells gave them similar visual appearance to the conventional monocrystalline cells. Eliminating color difference of multicrystalline cells is very beneficial for PV manufacturers, as the module price is largely dependent on the color uniformity. Structure-wise, the isotexture of a conventional cell has irregular pits in ~10 µm scale, while the nanotextured cell shows regular nanocones around 500 nm. This allows the SPERISE process to significantly reduce the amount of silicon consumed in the texturing process and enable a tighter process binning compared to the standard isotexturing. This also makes the nanotexturing highly amenable for the kerfless, thin wafering technologies in the roadmap.
Figure 3.8: The side by side comparison of commercial and nanotextured multicrystalline cells fabricated with the same batch of solar wafers. The SEM images show the surface texture of each corresponding cell.

We also found that the efficiency enhancement for multicrystalline cells was amazingly good, around 0.9% on average, while a 0.4% enhancement was achieved for monocrystalline cells (Fig. 3.9). The average peak efficiency of nanotextured multicrystalline cells was around 17.6%, which is in a high range among commercial cells. In addition to peak efficiency gain, the process variation (reflected by the standard deviation of cell efficiency) was also reduced. Statistical results show that the efficiency distribution of nanotextured cells is much narrower than the distribution of isotextured cells. This improvement was due to the higher structural uniformity of the surface textures in terms of height, size, and aspect ratio. Efficiency is the most important factor to determine the cell grade, and the cell grade determines the cell price. By increasing the mean value and decreasing the standard deviation, the problematic low-end tail
can be significantly reduced, which goes directly to the cell manufacturers’ revenue and profit margin.

**Figure 3.9:** Efficiency distribution of conventionally-isotextured and nanotextured multicrystalline cells. An efficiency boost of 0.9%, as well as tighter process binning, was observed with nanotextured wafers. The statistics were calculated with 100 cells of each type.

### 3.7 References


CHAPTER 4
NANOSTRUCTURED METALLIC NANOSURFACES

4.1 Fundamentals of nanoplasmonics

A plasmon is a density fluctuation of free electrons. When an external electromagnetic field (light wave) is incident on a metallic particle smaller than the incident wavelength, the incident electric field will displace the metal’s electron with respect to the lattice (Fig. 4.1a). Thus, an electromagnetic wave will produce an oscillating electron density known as localized surface plasmon (LSP) (Fig. 4.1b). LSP are also known as Mie plasmons as they have electric field closely related to Mie scattering [1].

Figure 4.1: (a) Sketch of a homogeneous metallic sphere placed into an electrostatic field. (b) Schematic diagrams illustrating of a localized surface plasmon (LSP).
The formulation of LSP in a single nanosphere starts from a solution of the Laplace equation for the potential, \( \nabla^2 \phi = 0 \), from which the electric field \( E = -\nabla \phi \) can be calculated [2], [3]. The general solution is of the form:

\[
\Phi(r, \theta) = \sum_{l=0}^{\infty} [A_l r^l + B_l r^{-(l+1)}] P_l(\cos \theta) \tag{4.1}
\]

The solution for the potentials \( \Phi_{\text{in}} \) inside and \( \Phi_{\text{out}} \) outside the sphere can be written as:

\[
\Phi_{\text{in}}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos \theta) \tag{4.2}
\]

\[
\Phi_{\text{out}}(r, \theta) = \sum_{l=0}^{\infty} [B_l r^l + C_l r^{-(l+1)}] P_l(\cos \theta) \tag{4.3}
\]

Determine coefficients \( A_l, B_l \) and \( C_l \) from the boundary conditions at \( r \to \infty \) and at the sphere surface \( r = a \); the potentials take the form:

\[
\Phi_{\text{in}} = -\frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 r \cos \theta \tag{4.4}
\]

\[
\Phi_{\text{out}} = -E_0 r \cos \theta + \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 a^3 \frac{\cos \theta}{r^2} \tag{4.5}
\]

From \( E = -\nabla \phi \), we get:

\[
E_{\text{in}} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 \tag{4.6}
\]

\[
E_{\text{out}} = E_0 + \frac{3n(n \cdot p) - p}{4\pi \varepsilon_0 \varepsilon_m} \frac{1}{r^3} \tag{4.7}
\]
\( \Phi_{out} \) describes the superposition of the applied field and that of a dipole located at the particle center. We can rewrite \( \Phi_{out} \) by introducing the dipole moment \( \mathbf{p} \) as

\[
\Phi_{out} = -E_0 r \cos \theta + \frac{\mathbf{p} \cdot \mathbf{r}}{4\pi \varepsilon_0 \varepsilon_m r^3} \tag{4.8}
\]

\[
\mathbf{p} = 4\pi \varepsilon_0 \varepsilon_m \alpha^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 \tag{4.9}
\]

\( \mathbf{p} = \varepsilon_0 \varepsilon_m \alpha E_0 \) by introducing the polarizability \( \alpha \):

\[
\alpha = 4\pi \alpha^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \tag{4.10}
\]

The above formula indicates that resonant enhancement happens at minimum \(|\varepsilon + 2\varepsilon_m|\), which is called Fröhlich condition and simplified as

\[
\text{Re}[\varepsilon(\omega)] = -2\varepsilon_m \tag{4.11}
\]

The associated mode is the dipole surface plasmon of the metal nanoparticle.

The Fröhlich condition expresses the strong dependence of the resonance frequency on the dielectric environment: The resonance red-shifts as \( \varepsilon_m \) is increased. Metal nanoparticles are thus ideal platforms for optical sensing of changes in refractive index. The resonance in \( \alpha \) also implies a resonant enhancement of both the internal and dipolar fields. It is this field-enhancement at the plasmon resonance on which many of the prominent applications of metal nanoparticles in optical devices and sensors rely.
The plasmon resonance is strongly dependent on particle shape and size, and on the coupling between particles. $\alpha$ can be reevaluated under different situations. For example, a general ellipsoid with semiaxes $a_1 \leq a_2 \leq a_3$, specified by $\frac{x^2}{a_1^2} + \frac{y^2}{a_2^2} + \frac{z^2}{a_3^2} = 1$, has the following expression for the polarizabilities $\alpha_i$ along the principal axes ($i = 1, 2, 3$):

$$
\alpha_i = 4\pi a_1 a_2 a_3 \frac{\varepsilon(\omega) - \varepsilon_m}{3\varepsilon_m + 3L_i(\varepsilon(\omega) - \varepsilon_m)}
$$

(4.12)

### 4.2 Fabrication of metallic nanosurface

This metallic nanosurface is fabricated with a high-density silicon nanocone array followed by an e-beam evaporation process (Fig. 4.2a). The silicon nanocone array is fabricated by a simultaneous bottom-up and top-down process discussed in our previous publication (Fig. 4.2b) [4]. To make the plasmonic black silver substrate, we deposit silver directly on top of the black silicon. 5-nm-thick titanium was deposited ahead of 80 nm thick silver as an adhesion layer in between silicon and silver. Due to the large slope of the sidewall (> 75°), instead of forming a uniform layer of silver film, the deposition of silver on silicon nanocone surface follows a fashion of Volmer-Weber growth forming isolated nanoparticles of around 50~nm in diameter [5]. The AgNPs on nanocone surface form two types of nanogaps: 1. inter-nanoparticle gaps on single nanocone and 2. inter-nanocone gaps between nanoparticles on adjacent nanocones.

**Figure 4.2c** shows the scanning electron microscope (SEM) image of the cross-section of the black silver substrate, in which we can see the darker silicon nanocone forest covered by a layer of brighter silver on top, especially on the tip of cones. The nanocones are around 200 nm
tall, 80 nm wide at the base. The spacing between two adjacent silicon nanocones without silver coating is about 100 nm and the spacing is reduced to sub-50 nm after silver coating.

**Figure 4.2:** (a) Schematic fabrication process of the NanoSERS substrate. (b) SEM image of the nanocones with the oxide balls on the top. (c) SEM image of the silver-coated nanocones.

### 4.3 Theoretical simulation of nanoplasmonic structures

The presence of SPR in our fabricated nanoplasmonic structure is independently verified by using two commercially available electromagnetic simulation packages (DIFFRACTMOD, RSoft Design, and COMSOL). DIFFRACTMOD uses rigorous coupled-wave analysis (RCWA) and can provide information about diffraction efficiency as a function of wavelength. The absorption maxima (or reflection minima) of the calculated spectra can be utilized to identify the resonant mode. For the RCWA simulation, we used a silicon cone structure with height 200 nm, base 120 nm, with a period of 300 nm. The silver layer on top of the silicon cones is 80 nm thick. The absorption efficiency (also the reflection efficiency) of the TM resonant mode was calculated in the wavelength range of 200<\(\lambda\)<900 nm and the incident angle was varied from
$0^\circ < \theta < 60^\circ$. **Figure 4.3a** presents the dispersion diagram of the aforementioned nanoplasmonic structure. The dispersion diagram clearly shows that the nanocone plasmonic substrate can support broadband SPR supporting many incident wavelengths in the range 200–700 nm covering various incident angles from $0^\circ$ to $60^\circ$. The electromagnetic field distribution within the nanocone plasmonic structure is simulated by COMSOL. The complex optical constants of silver and silicon are taken from Palik’s handbook [6]. **Figure 4.3b** shows the excited scattering field in TM mode for an incident wavelength of 785 nm. The different colors indicate the magnitude of the normalized amplitude of scattering electric field with respect to that of incident electric field, red indicating high field, and blue indicating low field [7]. Two different LSPR modes, namely, the “gap” mode (**Fig. 4.3c**) and the “tip” mode (**Fig. 4.3d**) can be clearly seen in the simulation. The gap mode is due to the confinement of electromagnetic field in close proximity ($<30$ nm) between two adjacent nanocone plasmonic structures. The field intensity is enhanced by up to $4 \times 10^4$ times as compared to the incident field intensity ($I_{\text{inc}} = |E_{\text{inc}}|^2$). The high electromagnetic field at the top of the nanocone structure is due to LSPR at the sub-20-nm silver nanobead structures, similar to LSPR observed for metallic nanoparticles [8]. The exponential decaying nature of the surface plasmon near-field away from the metal surface can be clearly seen in **Fig. 4.3d**.
4.4 Super-black metallic surface

In macroscale, we observed by naked eye that while silver-coated smooth silicon or the smooth silver substrate looks bright and shiny like a mirror, the silver-coated black silicon surface looks much darker and not shiny. For this reason we give it the name black silver substrate. To quantify the optical reflectance and absorbance of black silver substrates, we
measured and compared the reflectance spectra in the wavelength range from 200nm to 1100nm with a UV-Vis-IR optical spectrophotometer (Varian Cary 5G). According to Fig. 4.4, the distinction between reflectance on smooth silver, black silver and smooth silicon wafer is significant; the reflectance of smooth silver is above 80% while the reflectance of black silver is below 20% in the entire wavelength range. The reflectance of smooth silicon always resides in between the former two. The averaged reflectance over all wavelengths is 92.5% for smooth silver, 51.2% for smooth silicon and 9.9% for black silver. Since none of the substrates is transparent, we consider no optical transmission and the absorbance A = 1-R, where R is the reflectance. With this assumption, the averaged absorbance of black silver is 90.1%, 12 times higher than the averaged absorbance of smooth silver (7.5%), which agrees with the reported calculation earlier [9].

Figure 4.4: Reflectance spectra of black silver, smooth silver, and smooth silicon.

Since silver has been known to have low loss plasmonic resonance, we can assume that most of the incident photons are trapped in the silver-coated nanocone forest and converted to localized and surface plasmons, which is also indicated by the simulation result shown later. As the matter of fact, the reflectance from the black silver substrate is very different from the reflectance from the smooth silver substrate. For smooth silver substrate, the reflectance
primarily consists of specular and diffuse reflection of incident light while for black silver substrates the measured reflectance is actually the secondary scattering photon emission converted from the resonating plasmons on surface. The reason why the light “reflectance” of the black silver substrate is slightly higher than the corresponding black silicon substrate is due to the plasmon scattering from the silver material coated on the silicon nanocones.

4.5 Metal-enhanced fluorescence

To demonstrate fluorescence enhancement on the black silver substrate, we deposit R6g solution with the concentration of 10 μM on both black silver, smooth silver and glass slide, wait until dry and excite the fluorescence with green light (550 nm center wavelength). The image is taken with a microscope objective lens with 20× magnification and numerical aperture (NA) of 0.5. The intensity distribution is captured with a black and white CCD camera. In Fig. 4.5a, c, we present the pseudo-color fluorescence emission intensity image. Figure 4.5a is the intensity image taken on the square array patterned black silver substrate. Obviously, the intensity on the black silver square region is much higher than the surrounding smooth silver region, which is also illustrated in Fig. 4.5b, the intensity profile across the white dashed line in Fig. 4.5a. Figure 4.5c is the fluorescence intensity image on the edge of an R6g drop stain on uniform non-patterned black silver, in which the red region is covered by R6g and evident uniform molecule deposition ensures fair intensity measurement. From Fig. 4.5d, the comparison of fluorescence emission spectra over the entire microscopic field of view (400 μm × 400 μm) taken on uniform black silver, smooth silver and regular glass slide, all captured with the integration time of 5 seconds, we see the emission of R6g is much stronger on black silver than on smooth silver or glass slide. By subtracting the background from all the fluorescence spectra and dividing the area
under spectra curve from 600 nm to 700 nm on black silver by that on smooth silver and glass slide, we obtain the fluorescence enhancement on the black silver for 15 times with respect to smooth silver and 29 times with respect to glass slide. It is worth noting that the fluorescence enhancement on the photon trapping black silver substrate is an interesting observation. For most plasmonic metal nanostructures like silver or gold nanoparticle enhanced fluorescence, the fluorescence emission photon is not likely to be trapped as in the case of black silver substrate; therefore, almost 100% emission photons may be acquired in imaging process. However due to the highly efficient photon trapping property of black silver the fluorescence emission photons from R6g molecules should be mostly trapped within the nanocone forest without being acquired by the imaging or spectroscopy system. Even with such potential loss, we still observed ~30 times fluorescence enhancement. We provide two possible explanations: the first one is that the fluorescence emission photons from the R6g molecules are mostly converted into plasmons and later re-emitted into free space through the plasmon scattering which was accounted for by the 10% optical “reflectance” measured from the black silver substrate; the second explanation is that the cavity mode plasmon resonance and localized electromagnetic field in the silver-coated nanocone forest are extremely strong and can excite very high fluorescence emissions for which even a small portion of fluorescence emission photons escaping to the free space has much higher intensity than the fluorescence intensity on smooth silver or glass slide. Further theoretical investigation is underway.
Figure 4.5: (a) Fluorescent image on square array patterned black silver. (b) Intensity profile across the white dashed line on (a). (c) Fluorescence image on the edge of a R6g on a uniform black silver substrate. (d) Fluorescence spectra of R6g on smooth silver, glass slide and black silver.

4.6 Surface-enhanced Raman spectroscopy

All SERS spectra were taken with a sample-scanning Raman spectrometer system as described earlier (Fig. 4.6) [10]. The system comprised a semiconductor 785 nm CW diode laser, a microscopy system, a 3D scanning stage, and a thermoelectric-cooled (183 K) CCD camera (PIXIS-400, Princeton Instruments). The spectral resolution was approximately 1.5 cm$^{-1}$ in the near-infrared range. A 10x microscope objective lens (Mitutoyo infinity-corrected long working
distance objectives) with an effective focal length of 20 mm and diameter of 24 mm was used to focus the excitation laser beam onto the sample and to collect the backscattered radiation.

![Schematic of SERS experimental set-up](image)

**Figure 4.6**: Schematic of SERS experimental set-up. The SERS substrate is placed upside down and illuminated with a 785 nm CW diode laser. The scattering light is collected with a spectrometer.

The goodness or quality of a SERS substrate is universally characterized by a simple parameter called the enhancement factor (EF). Generally speaking, the enhancement factor quantifies the amplification of the Raman signal by the surface-enhancement effect of metallic nanostructures compared with normal Raman under the same experimental conditions. Therefore, the most straightforward and intuitive way to estimate enhancement factor is the following equation, which is called analytical enhancement factor [11]:

$$EF_a = \frac{I_{SERS}/c_{SERS}}{I_{RS}/c_{RS}}$$
where $I_{RS}$ and $I_{SERS}$ denote the Raman and SERS signal intensity at a single Raman shift, and $c_{RS}$ and $c_{SERS}$ are the molar concentration of the molecules on the reference sample and on the SERS substrate. However, this formulation does not consider the substrate surface topology and the coverage of adsorbed molecules.

To correct the calculation, more factors, such as laser spot size, surface area ratio, molecular coverage, need to be included in the equation. The most widely accepted enhancement factor definition is formulated from SERS substrate point of view [12]:

$$EF_s = \frac{I_{SERS}/N_{surf}}{I_{RS}/N_{vol}}$$

where $I_{RS}$ and $I_{SERS}$ denote the Raman and SERS signal intensity at a single Raman shift. It can be calculated by an integral of photon counts under a specific Raman peak. $N_{surf}$ and $N_{vol}$ are the number of molecules bound to the enhancing metallic SERS substrate and in the excitation volume respectively.

In the case of planar reference sample, $N_{vol}$ can be calculated by the following equation [13]:

$$N_{vol} = c_{RS}N_A \cdot \pi r^2 h$$

where $c_{RS}$ is the molar concentration of the molecules on the reference sample, $N_A$ is the Avogadro constant, $r$ is the radius of the excitation laser spot, and $h$ is the thickness of the molecule on the reference region.
Due to the randomness of the nanostructures, the probed molecule number $N_{surf}$ usually cannot be calculated accurately. It can only be estimated by considering the distributions of the nanostructures, the size and topology of the nanostructures, and the molecular concentration and coverage area [14]. A series of measurements, counting and assumptions regarding the nanostructures need to be made by the SEM or AFM imaging.

Following the above substrate-centric formulation, we choose the 1366 cm$^{-1}$ peak in r6g spectrum to calculate the enhancement factor. The SERS substrate used here is the pseudo-randomly distributed nanocone array covered Au nanoparticles. The nanocones have an average height of 600 nm and base diameter of 300 nm. Statistically, there are around 10 nanocones per $\mu m^2$ and 120 GNPs on each nanocone. The diameter of hemispherical nanoparticles is around 50 nm. Therefore, the surface area ratio can be calculated with the following equation:

$$m = \frac{A_{l \times l} - 10\pi r_{cone}^2 + 10n \cdot 2\pi r_{GNP}^2}{A_{l \times l}}$$

where $A_{l \times l}$ is the counting area, i.e., 1 $\mu m^2$, $r_{cone}$ and $r_{GNP}$ are the radius of nanocone base and the hemispherical gold nanoparticles. $m$ is calculated to be 5.

The 1 $\mu$M and 100 $\mu$M r6g were used for SERS and normal Raman measurements respectively, and the 1366 cm$^{-1}$ peak intensity $I_{SERS}$ and $I_{RS}$ are 2053 and 278 photo counts. The r6g spot sizes were 4 mm$^2$ and 1.8 mm$^2$ on the reference sample and SERS substrate. $N_{Vol} = 5.45 \times 10^{19}$ and $N_{surf} = 1.18 \times 10^{12}$. Therefore the calculated enhancement factor is $3.41 \times 10^8$. 

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4.7 High-uniformity molecular surface deposition

Interestingly, such silver-coated nanoconic surface topology drastically limited the spreading of liquid sample droplets, and also allowed exceptionally uniform molecular deposition, which is crucial for high quality molecular microarrays. The hydrophobic surface property with the liquid contact angle of 105° on the silver-coated nanoconic surface was not observed using other substrates commonly used for microarrays such as flat metal-coated chips or pre-treated glass slides. The side views of 100 μM fluorescent Rhodamine 6G solution droplets manually deposited on either silver-coated nanocone array substrate, or flat metal-coated substrate, or pre-treated glass (common substrates used in proteomics), are shown in Fig. 4.7a. Images were processed to measure and compare droplet contact angle (θ) and contact distance (L). The hydrophobicity is primarily attributed to the unique high aspect ratio, high density metallic nanoconic array structure, which allows for the ‘petal effect’ defined in the Cassie–Baxter model [15], [16]. As a matter of fact, similar microscale and nanoscale textures were exploited to create superhydrophobic or superoleophobic surfaces [17] although neither the molecule deposition nor the optical imaging application was thoroughly studied. In this case there is a nanoscale-thickness air layer beneath the liquid droplet where the localized liquid–solid interfaces are pinned on the side wall of the nanocones. Due to the extremely high hydrophobicity of air, the silver-coated nanocone surface is much more hydrophobic than the flat silver-coated substrate.
Figure 4.7: Liquid droplets and molecule depositions on various substrate surfaces. (a) Side view images of liquid droplets dispensed on the silver-coated nanocone substrate, flat silver surface, and pre-treated glass slide, respectively from left to right. The diameter (D) and contact angles (θ) of the liquid droplets are annotated. The water droplet contains 100 μM Rhodamine 6G (R6G) molecules. (b) Laser scanning fluorescence images of R6G molecules deposited on the above three kinds of substrate surfaces after the droplets dried. The boundaries of the main molecule deposition patterns are denoted by S and those of the peripheral deposition are denoted by S’. (c) A three-dimensional (3D) image representation to evaluate optical homogeneity of molecule deposition. Intensity profiles from two-dimensional (2D) images in (b) are converted to a 3D surface plot in which the height represents the fluorescence intensity or molecule density. (d) Fluorescence images of a 5 × 5 array of molecule deposition spots. Dimensions of deposition (spot center-to-center (D) and diameter (d)) are measured and annotated. The scale bar on the right represents 200 μm. (e) Array printing images on the silver-coated nanocone substrate with the spacing between spots of 200, 150, 100, and 50 μm from top to bottom. The scale bar on the top represents 1 mm distance.
As usual, using glass or metal-coated flat substrates resulted in the formation of irregular ‘coffee ring’ deposits which are confirmed by laser scanning fluorescence imaging (Fig. 4.7b, c). Optically dense wrinkles within a well-delineated area or ring patterns (marked by ‘S’) surrounded by an undefined deposition haze (marked by S’) (Fig. 4.7b) were evident for the molecular deposition spots on the glass slide surface in the surface plot of fluorescence intensity profiles. The multiple molecular deposition rings observed on the flat substrate surface are due to the receding solvent boundary having a few pinned positions on the surface in the drying process. In sharp contrast, when using a silver-coated nanocone substrate, ultrahigh homogeneity was obtained (Fig. 4.7c). The deposition assumed a disc-like shape, optically highly uniform, with >95% of all data points within the same range of fluorescence intensity (<5% variation), covering the smallest surface area, and leaving no peripheral background. Assuming the fluorescence intensity is proportional to the Rhodamine molecule density, the molecule deposition is extremely uniform with <5% variation. Based on the aforementioned mechanism for droplets in Cassie state, the molecules will stay on the sidewalls of the nanocones where the localized droplet pinning positions are. In fact there are still ‘coffee rings’ in this case; however, they are nanoscale local ‘coffee rings’ deposited on the sidewall of each nanocone rather than the global ‘coffee ring’ as seen in the case of flat surfaces. It should be noted that coexistence and transition between Cassie and Wenzel states could occur on a pillared hydrophobic surface [18]. At the Wenzel state the uniformity of molecule deposition on the nanocone array substrate after droplet drying may be lower as there will be little or no air gap beneath the droplet. However, in this case hindered molecule drift through high-density nanocones near the drying moment may also help reduce the coffee ring formation.
We confirmed the advantageous surface property of the silver-coated nanocone substrate also for the array of multiple droplets dispensed by an automated inkjet array printer. The tested water-based samples contain either Rhodamine dye molecules or peptides or detergents such as DMSO. Dimensions of deposition such as spot diameter (d) and center-to-center distance (D) were measured after printing the Rhodamine 6G solution on the surface. The best spotting density avoiding merging of droplets happened when using silver-coated nanocone arrays, whereas metal-coated flat surfaces could not support spotting of 80 pl droplets less than 150 μm apart, as shown in the laser scanning fluorescence image (Fig. 4.7d). Merging of some contiguous spots could be observed on the flat silver-coated substrate, while spots systematically merged when deposited over the glass slide surface at such high spotting-density resolution. In sharp contrast, no droplet merging was observed on the silver-coated nanocone substrate under similar deposition conditions (volume 80 pl/d = 150 μm/D = 150 μm which is considered as medium to high deposition density). Other conditions were also tested (Fig. 4.7e). Using the same automated printing instrument, the finest spot dimensions we systematically and safely reached and observed without any merging were: d = 500 μm/D = 1 mm for glass (∼1.78 spots mm⁻²), d = 250 μm/D = 500 μm for flat silver-coated substrate (∼7.11 spots mm⁻²), and d = 80 μm/D = 100 μm for silver-coated nanocone substrate (∼123.45 spots mm⁻²). We estimated that easily 10 to at least 50 times more samples per unit area could be reliably deposited using robots on the metallic nanocone array surface in comparison to smooth metallic substrates or glass. The homogeneity and density of molecular deposition were dramatically improved for high quality optical molecular imaging when using the ‘coffee ring’-free surface. Although not shown here, a similar test on gold-coated nanocone devices was also conducted and we observed similar surface properties with uniform molecule deposition.
4.8 References


CHAPTER 5

ELECTRICALLY INDUCED CONFORMATIONAL CHANGE OF PEPTIDES ON METALLIC NANOSURFACES

5.1 Introduction

The responses of biomolecules to external stimuli are the focus of many studies and applications in biomedicine. Physical stimuli, such as mechanical [1], thermal [2], optical [3], and electrical ones [4], alter and manipulate energy, composition, structure, and conformation and, thus, change and control function and activity of biomolecules. For example, molecular switches can be reversibly shifted between two or more stable states in response to external stimuli, such as force [5], temperature [6], light [7], and electrical potential [8]. Most of the manipulations, especially mechanical and electrical ones, are mediated by a molecule–solid interface [1], [4], [5], [7], [8].

Biological and chemical stimuli, such as pH variation [9], microenvironment change [10], and the presence or absence of a ligand [11], can also induce compositional and structural changes to molecules in a biomimetic system, such that these molecules can act as sensors [12], [13] as long as the intermolecular or intramolecular effects can be detected and reported. On the basis of this idea, various lab-on-a-chip devices [14] have been created, such as DNA [15], protein [16], and antibody [17] microarrays, and numerous spectroscopic techniques have been adopted, such as fluorescence [18], vibrational [19], and nuclear magnetic resonance [20], to detect and monitor the conformational change in biomolecules.
In the present study, we employ surface-tethered peptide probes for kinase enzymes to demonstrate in an exemplary fashion electrical manipulation and spectroscopic detection of intramolecular conformational change in the sub-nanometer range possible today. The function of kinases is to activate other proteins through phosphorylation, i.e., through transfer of a phosphate group (PO$_3^{2-}$) from ATP to proteins, usually on serine, threonine, or tyrosine residues. Disruptions of kinase signaling pathways are frequent causes for diseases, such as cancer and diabetes [21]. The various conformations of peptide probes with or without phosphorylation arise from the charges of the ionized phosphate groups added by kinases as well as from the interaction with the charges on the nanostructured surface material. If an electric field is applied across the peptide probes, either phosphorylated or not, the probe’s conformation will be altered due to the electrostatic force and the structural difference between a peptide probe with and without a phosphate group will be amplified. In particular, the relative distance between the phosphorylated residue in the peptide probe and the nanostructured surface material will be influenced significantly. In our study, this distance change is detected by a near-field optical detection method, surface-enhanced Raman spectroscopy (SERS), in which the signal intensity is inversely proportional to the 12$^{th}$ power of the distance between chemical analyte and nanostructured metallic surface [22]. To elucidate the actual conformational changes that occur, and to interpret the experimental findings, molecular dynamics (MD) simulations are carried out to visualize the structural dynamics of the attached peptide probes. Through the combined effort of experiments and simulations, we study the details of peptide conformational change on nanostructure surfaces as well as propose a highly sensitive sensor for detecting changes in molecular conformation.
5.2 Control of molecular conformation with electric field

In a previous study [23], it was shown that a Schottky junction can be formed between adsorbed molecules and a metal surface. The underlying near-field interaction not only is a likely contributing factor for SERS but also modifies the charge distribution of attached molecules. In free solution, charge distribution and conformation of molecules are determined by the ion species and pH value of a buffer solution; however, the strong charge interaction between molecules and a metallic surface [24] provides a route to control the conformation of the molecules by changing the charge distribution of the metallic surface, which is achievable through application of an electric potential. Here, we employ a synthetic peptide sequence and its phosphorylated counterpart as exemplary small molecules as well as a gold surface connected to a dc power source (Fig. 5.1a).

The peptide sequence employed (EGIYGVLFKPKC) is a commercially available kinase profiling peptide substrate [25]. The oligopeptide contains a tyrosine at position 4, a target for phosphorylation by Src kinase (Fig. 5.1b). The N-terminus is labeled with rhodamine 6G (rho) to permit a spectroscopic response. The C-terminus includes a cysteine used to attach the peptide to the gold surface through a gold–thiol bond. The gold surface, as the bottom electrode, is connected with an indium tin oxide (ITO) top electrode through a dc power source to form a parallel-plate capacitor. By applying a dc voltage to the capacitor, the gold surface is biased positively or negatively with measurable charge densities (Fig. 5.1c,d). The non-phosphorylated sequence used here is nearly neutral in buffer solution. Phosphorylation of peptides with isoelectric point pI > 7.0 usually results in a large shift of pI to lower values [26], and in the present case, the phosphate group added to the tyrosine at position 4 introduces a net negative
charge of $-2e$; therefore, the peptide conformation becomes responsive to the surface charge. On a positively charged metal surface with electric field pointing toward the top ITO electrode, the non-phosphorylated peptides experience minimal conformation change (Fig. 5.1c), while the phosphorylated ones bend toward the gold surface (Fig. 5.1d).

**Figure 5.1**: Electrical control of molecular conformations through a charged metal surface. (a) Highlighted in the front is an atomic model of the peptide-\textit{rho} system tethered to the gold surface colored in yellow. This surface is assumed to be planar at the 10.2 nm × 10.2 nm scale simulated. Other peptide probes are colored in green. The front peptide is highlighted in licorice representation; carbon atoms are colored in light blue, nitrogen atoms dark blue, oxygen atoms red, and phosphate atoms yellow; for the sake of clarity hydrogen atoms are not shown; blue and red arrows point to the \textit{rho} cap and the phosphorylated tyrosine residue, respectively. (b) Kinases or phosphatases add or remove a phosphate group to (on) the peptide probes and thus modify the net charge of the probes. The peptide is represented as a green line, the phosphate group as a red dot, and the \textit{rho} fluorescence probe as a blue star. (c) Non-phosphorylated peptides are nearly neutral and unaffected by charges on the metal surface. (d) Phosphorylation introduces a net charge of $-2e$ to the peptides, which leads to bending of the peptides under positive surface charge polarity.
The conformational changes mentioned above can be experimentally detected in situ by monitoring SERS signal changes under different electric fields. The distance change between the free end of the peptide and the gold surface, reflecting peptide stretching or coiling, can also be captured from the different measured SERS signal intensities. To enhance this spectroscopic signal, we employ a high-quality gold-coated SERS substrate as shown in the schematic drawing and SEM image (Fig. 5.2a,b). This device is a high-density silicon nanocone array coated with gold nanoparticles (GNPs). The silicon nanocone array is fabricated by a simultaneous bottom-up and top-down process discussed in a previous publication [27]. The GNPs are created by an e-beam evaporation process. Due to the large slope of the sidewall (>75°), instead of forming a uniform layer of gold film, the deposition of gold on the silicon nanocone surface follows a kind of Volmer–Weber growth, forming isolated nanoparticles of around 50 nm in diameter [28]. The GNPs on the nanocone surface form two types of nanogaps: (i) inter-nanoparticle gaps on single nanocones and (ii) inter-nanocone gaps between nanoparticles on adjacent nanocones. Thus, compared with conventional two-dimensional metallic nanoparticle arrays, the present device has a much higher SERS hot-spot density, resulting in much higher SERS sensitivity. In a previous study [29], we have demonstrated similar substrates with an enhancement factor of $10^8$–$10^9$ to Raman signals.

Figure 5.2a illustrates our phosphorylated peptide–GNP conjugation system at the nanoscale. An enhanced localized electrostatic field pointing in two opposite directions can be formed by cumulated negative or positive charges on each individual GNP surface (Fig. 5.2c). The strength of the electrostatic field can be controlled by changing the size of the GNPs (Fig. 5.2d). The electric field component orthogonal to the gold surface induces, depending on sign, stretching or coiling of the phosphorylated peptides (Fig. 5.2a), which attenuates or amplifies the
SERS signal following the aforementioned 12\textsuperscript{th} power law. Conversely, non-phosphorylated peptides carrying no extra charge should contribute with a constant, namely, field-insensitive Raman scattering signal.

**Figure 5.2:** Topology of experimental nanodevice. (a) Schematic drawing of GNP-coated nanocones and surface-tethered peptides. GNP are colored in yellow; peptides in blue. SERS signals are attenuated or amplified when peptides stretch or coil under different surface charge polarities. (b) Scanning electron microscope image showing silicon nanocone array with uniformly coated GNP at the tips and sidewalls. (c) Calculated enhancement of electrostatic field near a GNP-coated silicon nanocone surface. The GNPs on the top and sidewall of the nanocone are 90 and 50 nm in diameter, respectively. The top electrode is 1.5 μm away from the bottom surface. The electric field near the GNP surface reveals a high-field gradient near the tethered peptides. The maximum field strength is $7.33 \times 10^6$ V m\textsuperscript{-1} and arises near the top of the nanocones. The yellow arrows represent the electric field directions and strength. (d) The dependence of the maximum local electrical field intensity near the sidewall GNP surface on the diameter of GNPs. The results show stronger localized electrical field for larger GNPs.
5.3 Characterization of nanoplasmonic sensor and electrically-amplified SERS spectra

We first tested the Raman profiling capacity of the SERS substrate. We found that Raman signals of rho molecules and surface-tethered peptides, indeed, were greatly amplified, easily detectable, and unambiguously discernible (Fig. 5.3). Figure 5.3a shows the representative SERS spectra of rho molecules at different concentrations, corresponding to the molecular monolayers with different surface coverage ratios. The relative intensities of SERS signals decreased linearly with serially diluted rho solutions [30]; however, the primary Raman peak signature of rho was still clearly identifiable at a concentration as low as 1 pM (1 part per billion), indicating the ultrahigh sensitivity of the SERS substrate. This prompted us to test whether the substrate is sensitive enough to distinguish the rho molecules, rho-labeled phosphorylated peptides (rho-EGI(pY)GVLFKKKC), and rho-labeled non-phosphorylated peptides (rho-EGI(Y)GVLFKKKC). As seen in Fig. 5.3b, compared with the spectrum of rho molecules, some additional Raman peaks appeared in the peptide SERS spectra. We also found that specificity and magnitude of SERS signals were significantly altered between the phosphorylated and non-phosphorylated states. Other peptide sequences, including ones previously used in tyrosine-kinase assays (IYGEFKKKAAC) [31] or known as regulatory sites of oncogenic Src kinases (IEDNEYTARQGGC), were tested and reported in previous work [32], [33]. Altogether, the experiments confirmed that our substrate is sensitive enough to capture a SERS signal difference due to a change in peptide phosphorylation state.
Figure 5.3: SERS sensitivity for phosphorylation detection. (a) Representative SERS spectra of serially diluted rho solutions spotting on the substrate surface. Concentrations from 100 μM down to 1 pM were faithfully detected, displaying a sensitivity down to 1 part per billion. (b) Comparison of SERS spectra for rho, rho-labeled non-phosphorylated, and rho-labeled phosphorylated peptide sequences, all in aqueous solution. SERS peaks are labeled by corresponding wave numbers; the latter are assigned to specific vibrations in Table 5.1. The spectra are equally offset in the plot in order to display all spectra clearly.

Table 5.1 lists the vibrational band assignments for the SERS spectra shown in Fig. 5.3b. Complete assignment is difficult due to the specific peptide sequence, metallic nanostructures, and surface chemistry, but the above assignment is sufficient to show differences between three molecules. As seen in Table 5.1, Raman peaks of the two peptides can be aligned with rho vibrational bands as they arise in the SERS spectra of rho. As expected, additional peaks arise in the SERS spectra of the peptides, corresponding to the vibrational modes of peptide chemical bonds and possible secondary structures. Specifically, tyrosine, phenylalanine, and cysteine vibrations can be identified clearly. Noteworthy are significant peak shifts (highlighted in orange) and peak intensity changes (highlighted in blue) between the phosphorylated and non-phosphorylated peptides. As mentioned before, phosphorylation can result in significant shifts of pI value, and can thus induce noticeable conformation changes. One evidence for this is that two
small SERS peaks at 1273 cm\(^{-1}\) and 1297 cm\(^{-1}\), corresponding to the amide III mode and indicating formation of α-helix, are not seen in the spectrum of the phosphorylated peptide, i.e., the α-helix might be disrupted after the phosphorylation. Several new peaks in the SERS spectrum of the phosphorylated peptide, such as 516 cm\(^{-1}\) and 1017 cm\(^{-1}\), might stem from the phosphate group.

As illustrated in Fig. 5.1c,d, application of an electric field orthogonal to the nanochip should bend the peptides toward the gold surface or stretch them away from it. Due to the charge [24] or electromagnetic [46] coupling effect, the SERS signal is very sensitive to the distance between peptides and the gold surface [22], and a significant SERS variation is expected for even a slight conformational change. The averaged SERS spectra for non-phosphorylated and phosphorylated peptides are shown in Fig. 5.4a and b, respectively. The spectra were measured under 0, ±1.2 V conditions. For the non-phosphorylated peptide probe, the SERS signal intensity did not register an observable change under different voltage conditions; however, for the phosphorylated peptide probe, the SERS signal intensity exhibited a significant change, namely, a higher signal for positive electric field and a lower one for negative electric field. The standard deviation around the mean (area plot under SERS spectra) is less than 10%, demonstrating the systematic character of conformational changes under electric field conditions.
Table 5.1: Band assignments for SERS spectra of \textit{rho}, \textit{rho}-labeled non-phosphorylated sequence, and \textit{rho}-labeled phosphorylated sequence.

<table>
<thead>
<tr>
<th>Raman Shift (cm(^{-1}))</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{rho} \ 516</td>
<td>Phosphate group</td>
<td>34</td>
</tr>
<tr>
<td>\textit{rho-Y} \ 529</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho-pY} \ 529</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\ 527</td>
<td>Phosphate group</td>
<td>34</td>
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<tr>
<td>\ 576</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho} \ 578</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho-Y} \ 619</td>
<td>R6G, C–C ring in-plane bending</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho-pY} \ 619</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\ 619</td>
<td>R6G, C–C ring in-plane bending</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\ 627</td>
<td>Tyr</td>
<td>42, 43</td>
</tr>
<tr>
<td>\ 642</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho} \ 644</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho-Y} \ 665</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho-pY} \ 664</td>
<td>R6G</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\ 667</td>
<td>R6G, C–C ring in-plane bending</td>
<td>35 - 37</td>
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<tr>
<td>\ 727</td>
<td>Tyr</td>
<td>42, 43</td>
</tr>
<tr>
<td>\ 778</td>
<td>R6G, C–H out-of-plane bending</td>
<td>35 - 37</td>
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<td>R6G</td>
<td>35 - 37</td>
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</tr>
<tr>
<td>\textit{rho-pY} \ 831</td>
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<td>42, 43</td>
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<tr>
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<td>R6G</td>
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<tr>
<td>\ 874</td>
<td>Cys</td>
<td>38 - 41</td>
</tr>
<tr>
<td>\ 893</td>
<td>Cys</td>
<td>38 - 41</td>
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<tr>
<td>\ 931</td>
<td>Phe</td>
<td>38 - 40, 44</td>
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<td>\ 986</td>
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<td>\ 1017</td>
<td>Phe</td>
<td>38 - 40, 44</td>
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<td>\textit{rho} \ 1035</td>
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<td>38 - 40, 44</td>
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<td>35 - 37</td>
</tr>
<tr>
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<td>R6G</td>
<td>35 - 37</td>
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<td>R6G</td>
<td>35 - 37</td>
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<td>R6G</td>
<td>35 - 37</td>
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<tr>
<td>\ 1190</td>
<td>R6G</td>
<td>35 - 37</td>
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<tr>
<td>\ 1248</td>
<td>Amide III, (\alpha)-helix</td>
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<td>Amide III, (\alpha)-helix</td>
<td>45</td>
</tr>
<tr>
<td>\ 1297</td>
<td>R6G, Aromatic C–C stretching</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\textit{rho} \ 1316</td>
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<td>35 - 37</td>
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<tr>
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<td>35 - 37</td>
</tr>
<tr>
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<td>35 - 37</td>
</tr>
<tr>
<td>\ 1366</td>
<td>R6G, Aromatic C–C stretching</td>
<td>35 - 37</td>
</tr>
<tr>
<td>\ 1419</td>
<td>Tyr</td>
<td>42, 43</td>
</tr>
<tr>
<td>\ 1422</td>
<td>Tyr</td>
<td>42, 43</td>
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<tr>
<td>\ 1446</td>
<td>R6G, Aromatic C–C stretching</td>
<td>35 - 37</td>
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<td>\textit{rho} \ 1512</td>
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<td>\textit{rho-Y} \ 1567</td>
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<td>\textit{rho-pY} \ 1576</td>
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<tr>
<td>\ 1603</td>
<td>Tyr</td>
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<td>\ 1617</td>
<td>Tyr</td>
<td>42, 43</td>
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<td>\ 1650</td>
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<td>35 - 37</td>
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<tr>
<td>\textit{rho-Y} \ 1692</td>
<td>R6G, Aromatic C–C stretching</td>
<td>35 - 37</td>
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<tr>
<td>\textit{rho-pY} \ 1690</td>
<td>R6G, Aromatic C–C stretching</td>
<td>35 - 37</td>
</tr>
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</table>
The averaged SERS spectra under 0, ±1.2 V conditions are shown color-coded at the top of Fig. 5.4c and d for non-phosphorylated peptides and phosphorylated peptides, respectively. The color coding allows rapid visual assertion of similarities and/or differences of SERS signals in side-by-side comparison. As one can see in Fig. 5.4c, in the case of non-phosphorylated peptides, the three spectra are extremely similar in peak (red) and valley (green) locations and intensities. However, in Fig. 5.4d, a clear difference in the color pattern can be discerned in the case of phosphorylated peptides with a mostly red (high intensity for +1.2 V) and green (low intensity for −1.2 V) SERS profile. The similarities and/or differences can be further confirmed by calculating the Log2-fold variation of the SERS signal at ±1.2 V relative to the original 0 V state, as can be seen in the bottom two lanes of Fig. 4c,d. For non-phosphorylated peptides, the variations are within ±σ (standard deviation) bounds, actually close to 0 at most Raman shifts. In contrast, for phosphorylated peptides the Log2-fold variations under +1.2 V are close to +1.5σ (red color) at most Raman shifts, and those under −1.2 V electric field are close to −1.5σ (blue color).
Figure 5.4: SERS spectra and statistical analysis of peptide probes for different voltages. (a, b) Averaged raw SERS spectra and standard deviation (area plot below each spectrum) of non-phosphorylated (a) and phosphorylated (b) peptide probes under 0, ± 1.2 V bias. The spectra are equally offset in the plot in order to display all spectra clearly. (c, d) Color-coded mean SERS spectra of non-phosphorylated (c) and phosphorylated (d) peptide probes under 0, ± 1.2 V bias (top three lanes) along with the Log2-fold variations of SERS spectra intensity with and without applied electric field (bottom two lanes). In (a) and (b), Raman shift is represented linearly in the range 500 to 1700 cm\(^{-1}\). Raman signal intensity and Log2-fold variations are represented by a color scale ranging from green to red (0–150 (c) and 0–385 (d)) and from blue to red (−1.0 to +1.0 (c) and −1.5 to +1.5 (d)), respectively, as shown by color bars (in units of standard deviation shown in a, b).
5.4 Unattended detection of kinase activities

Further, we demonstrate the capability of unattended detection of kinase activities. This study establishes a proof-of-concept for high throughput profiling of real patient samples. The methodology proposed here is to apply a random sequence of voltage stimulations at three states (e.g., +1.2 V is high, 0 V is medium, and -1.2 V is low) to each incoming sample, with long enough time interval (≥ 1 µs) for SERS measurement. The order of voltage stimulations is random; however the numbers of stimulations at three states are predetermined by a computer-generated three-digital code (l-m-n). One SERS measurement is performed and the spectrum is recorded after each voltage stimulation. After all measurements are done, an unsupervised hierarchical clustering (UHC) will be performed for the l+m+n measurements. A dendrogram will be generated based on the correlation of datasets, grouping most similar profiles with each other, and placing unrelated or most different samples away from best correlated datasets. This will give us a recovered three digital code (x-y-z), representing the number of spectra with high, medium, and low signal intensities respectively. As shown by Fig. 5.4, non-phosphorylated peptides (kinase reaction not happened) are unresponsive to electric field direction, and the SERS signal intensity variations are completely induced by the random motion of peptide probes. In contrast, the intensity variations for phosphorylated peptides (kinase reaction happened) exactly follow the directions of electric field. The probability that UHC code (x-y-z) of non-phosphorylated (phosphorylated) peptides exactly matches (does not match) with the original three digital code (l-m-n) is extremely small. Therefore, even for kinase at extremely low concentration, as long as the SERS signal variation follows (or does not follow) the voltage polarity, UHC operation will produce matched (or mismatched) code and allow the correct detection of kinase reaction.
An exemplary experiment is shown in Fig. 5.5. 30 SERS spectra of non-phosphorylated peptides (Fig. 5.5a) and phosphorylated peptides (Fig. 5.5c) under a random sequence of voltage stimulations are vertically plotted with color-coding, with 10 states at each of 0, -1.2 V. The voltage sequence represents a three digital code (10-10-10) applied to the sensor. Fig. 5.5b,d show the UHC results of the SERS spectra of non-phosphorylated peptides and phosphorylated peptides respectively. As shown in Fig. 5.5b, the UHC operation for SERS spectra of non-phosphorylated peptides could not recover the original code (10-10-10) carried by the voltage stimulations, indicating that the SERS signal intensity variations of non-phosphorylated peptides are random. In contrast, as shown in Fig. 5.5d, the recovered code for phosphorylated peptides is (10-10-10), which faithfully matches with the original code (10-10-10), indicating the phosphorylated peptides exactly follow the sequence of voltage stimulations.
Figure 5.5: Unattended detection of kinase activities by unsupervised hierarchical clustering (UHC). (a) SERS spectra of non-phosphorylated peptides under a random voltage sequence at 0, -1.2 V. 30 SERS spectra were shown vertically with color-coding, corresponding to the 30 voltage stimulations. (b) The results of unsupervised hierarchical clustering for the 30 SERS spectra shown in (a). (c) SERS spectra of phosphorylated peptides under a random voltage sequence at 0, -1.2 V. 30 SERS spectra were shown vertically with color-coding, corresponding to the 30 voltage stimulations. (d) The results of unsupervised hierarchical clustering for the 30 SERS spectra shown in (c).
5.5 Molecular dynamics simulation

The above results demonstrate that the presence or absence of phosphate groups on peptide probes is easily identified spectroscopically on the metallic nanosurface through SERS signal amplification or attenuation. MD simulations were performed to validate the interpretation of SERS signals at atomic resolution. However, such simulations suffer from a limitation in the accessible time scale. Current simulations cover typically only hundreds of nanoseconds, which is not long enough to explore low voltage-induced bending/stretching of peptides. To circumvent this problem and speed up the molecular responses, high-voltage biases were employed (the issue is discussed further below). In the simulations we also chose to describe the gold surface to which the peptides were tethered as planar, while it actually has some degree of curvature (Fig. 5.2). On the scale of the 10.2 nm × 10.2 nm area simulated, it is reasonable to assume a planar surface considering the much larger size (50 nm) of a single GNP (Fig. 5.2b). Other limitations intrinsic to our MD simulations are force field quality and system size simulated [47], [48]. Even though the outcome of MD studies is affected by those limitations, the MD simulations carried out should provide a valuable qualitative description of the peptide dynamics experienced by the real device [49]-[52].

We simulated two systems, each system composed of 25 peptides, the peptide sequence being the same as in the experiments. The C-terminus was attached to the gold surface, while the N-terminus was linked to a rho molecule. The sole difference between the two systems simulated is the phosphorylation of the tyrosine residue at position 4. We applied external electric fields and monitored the conformation of the peptides. Initially, ±6 V voltage biases were applied. Figure 5.6a,b show the average distance between the planar surface and the phenol oxygen of
tyrosine for non-phosphorylated and phosphorylated sequences. The non-phosphorylated peptides are insensitive to the applied biases. For the phosphorylated peptides, we observed a small response for different voltage polarities. In order to speed up the response we increased the bias to ±60 V. In an additional calculation (see Fig. 5.2c,d), we established the electric field around an actual GNP-coated nanocone surface, expecting that the field is not spatially homogeneous. We found that the electrostatic field focuses near the surface of the GNPs, giving rise to a high-field gradient near the peptides, the value of which corresponds roughly to the field arising near a flat model surface at ±60 V biases. This result suggests that the high bias assumed in the simulation may actually reflect values near the tethered peptides.

Figure 5.6c,d show the distance between tyrosine and gold surface for ±60 V biases for non-phosphorylated and phosphorylated sequences. For non-phosphorylated peptides, the results for ±60 V (Fig. 5.6c) are similar to the results for ±6 V (Fig. 5.6a); that is, the degree of peptide stretching is not affected by the applied field. Conversely, conformations of phosphorylated peptides depend on the voltage polarity. It is evident from Fig. 5.6d that tyrosine–gold distances converged to either complete stretching (−60 V, red line) or complete bending (+60 V, blue line) values. Figure 5.6i and ii present snapshots of the final conformation after 5 ns of MD simulations. The negative charge of phosphorylated tyrosine influenced the peptide conformation, inducing stretching for negative voltages (Fig. 5.6i) and coiling for positive ones (Fig. 5.6ii).

MD simulations confirmed the key interpretation of SERS spectra given above, namely, that phosphorylated peptides change their conformations under applied electric fields, while non-phosphorylated peptides remain insensitive to such fields. The MD results suggest, therefore,
that the peptide-conjugated nanosurface we created is an ideal electrophotonic molecular conformation sensor to detect phosphorylation and, thus, capture protein kinase activity.

**Figure 5.6:** Bending and stretching of phosphorylated peptides revealed by MD simulations. (a–d) Average tyrosine–gold distance of 25 peptides tethered to a planar gold surface. Error bars represent ±standard deviation. Non-phosphorylated peptide sensor under 0, ±6 V bias (a) and under 0, ±60 V bias (c). Phosphorylated peptide sensor under 0, ±6 V bias (b) and under 0, ±60 V bias (d). Panels (i) and (ii) show snapshots of peptide conformations after 5 ns for −60 V (i) and +60 V (ii) biases. The peptides are colored in gray, and tyrosine residues in red. Rhodamine residues are not shown. The 25 peptides were aligned using the attaching gold atom, shown in yellow. Grid spacing is 1 nm.
5.6 Sequence optimization of peptide nanoprobe

The MD simulations also revealed possible impediments to sensor performance; this information can be used to optimize sensor characteristics. First, we observed in all simulations aggregation of rho residues into dimers and trimers (Fig. 5.7a). Even though clotting of rho does not affect peptide stretching, it does reduce the accessibility of tyrosine residues, which is of critical importance for a functional device. Second, simulations showed that the three lysines at positions 9 to 11 (see Fig. 5.7b,c) are actually not required in our device; in microfluidic electrophoresis uses of the peptides, these positively charged lysines drive the non-phosphorylated peptides in the opposite direction from the negatively charged phosphorylated ones [25].

The MD results, then, suggested two improvements of the peptide used. First, the rho residues should be removed to avoid aggregation. Fortunately, rhodamine end groups are not required, as the spectroscopic signal depends on SERS and not on metal-enhanced fluorescence. Second, the lysine residues should be replaced by small, noncharged residues, as the aliphatic lysine tails adhere to the gold surface as well as to other peptide residues. Accordingly, we propose, based on the MD results, the modified sequence EGIYGVLAAC, which preserves the active sequence positions 1 to 7 (EGIYGVL), removes rho, replaces lysines with alanines, the later one being small residues that do not bind gold [53], and replaces phenylalanine at position 8 by alanine. The proposed sequence was tested using MD simulations at ±60 V. The simulated response is optimal: non-phosphorylated peptides are insensitive to voltage biases (Fig. 5.7d); phosphorylated peptides respond sensitively to voltage polarity (Fig. 5.7e). The suggested
sequence still needs to be bench-tested for SERS; but if successful, it will overcome shortcomings of the initial design.

Figure 5.7: Characteristics of initial and optimized sequences revealed by MD simulations. (a) Aggregation of three rho residues of non-phosphorylated peptides at 0 V. Aggregation of rho was observed in all MD simulations of the initial sequence. (b, c) Orientation of lysine residues of a non-phosphorylated peptide under +60 V and −60 V biases, respectively. Positively charged lysine residues respond to the external electric field; blue arrows highlight lysine direction. Positively charged residues are colored in blue, tyrosine in green, and negatively charged residues in red. (d, e) Response of the proposed new sequence (EGIYGVLAAAAC) to 0, ±60 V. The non-phosphorylated new sequence is insensitive to an electric field (d) and, when phosphorylated, is highly responsive to an external electric field (e). Error bars represent ±standard deviation.
5.7 Conclusion

We studied the electrostatic interaction between surface-tethered peptides and a metallic nanosurface. By altering the surface charge polarity and electrostatic field near the surface, we were able to induce peptide conformational changes, i.e., stretching or coiling. The sub-nanometer conformational change was greatly amplified and measured by a distance-dependent near-field optical detection method, surface-enhanced Raman spectroscopy. This method was shown to also clearly identify the phosphorylation state of the peptide probes through SERS signal variations upon application of different polarized electric fields. The method is sensitive enough to permit reliable identification of other charge-related biomolecule conformations on metallic nanosurfaces. The peptide–surface interactions underlying the method were elucidated at the atomic level by MD simulations, which support the interpretation of our SERS spectroscopy results. MD simulations also suggest a new peptide sequence to further improve the performance of the suggested device. The experimental and simulation results of our study establish a proof-of-concept for novel nanophotonic peptide phosphorylation sensors to be employed for high-throughput, high-sensitivity kinase profiling. In addition, the demonstrated electro-optical experiment and MD simulation approach should be widely applicable for the development of molecular level bio–nano interface interactions in general.
5.8 References


CHAPTER 6

ULTRAHIGH THROUGHPUT ADDITIVE NANOMANUFACTURING BY NANOTIP-ENHANCED ELECTROCHEMICAL 3D PRINTING

6.1 Introduction

In the era of “smart everything”, the pressing demand of miniaturization, integration, speed, and functionality of nanoscale devices, including integrated circuits, magnetic, optical, photonic, fluidic devices, MEMS/NEMS devices, biochips and biosensors, continuously pushes the limits of nanomanufacturing in terms of dimension, scale, cost, and throughput. Despite the attempt of the optical lithography industry to extend its capability by continuously reducing the wavelength of the light sources to overcome the resolution limit, the engineering challenges, complexity, cost, and footprint of the manufacturing equipment increase exponentially. Currently, the cost of lithography is more than 50% of the entire device fabrication; therefore, continuous innovation is necessary to drive down the cost, increase the throughput, and improve the reliability of the nanolithography process. The research community has been relentlessly exploring non-optical alternatives as the candidates for next generation lithography [1], such as electron beam, ion beam, X-ray, nanoimprint, and soft lithography. Tip-based nanolithography is a unique and important candidate among these next generation nanolithography technologies. Tip-based nanolithography refers to the technologies which use a functionalized microscopic or nanoscopic stylus as a “pen” to write nanoscale patterns constructively or destructively on the rigid planar surfaces with electrical, chemical, mechanical, or thermal processes [2]. Some noteworthy breakthroughs in tip-based nanolithography include “dip-pen” nanolithography (DPN) [3], which uses AFM tip as a “pen” to transfer “molecular inks” or “liquid inks” to the
substrate with a nanometer scale resolution, local oxidation nanolithography (LON) [4], which uses a positively-biased AFM tip to create a local oxidation at the tip-substrate interface in a water meniscus, and thermochemical nanolithography (TCNL) [5], which uses a heated nanotip to thermally activate chemical reactions on the surface and create patterns at nanoscale. Tip-based nanolithography has many advantages over conventional optical nanolithography, including unique atomic scale manipulation capabilities, versatility in fabrication processes and material selections, and low equipment, facility and energy budget. However, three major constraints and challenges [6] prohibit this technology from being considered as the candidate of next generation nanolithography, i.e., its low repeatability and reliability, its limited capability of creating truly three-dimensional nanostructures, and its low throughput and compatibility with parallelization.

In this chapter, we address the above challenges by introducing a nanotip-enhanced electrochemical 3D transfer printing process (named 3D Nano-TEEP) that enables ultrahigh throughput additive nanomanufacturing of truly three-dimensional nanoparticle arrays with excellent fidelity and resolution. The 3D Nano-TEEP is a highly-parallel nanomanufacturing process deploying a whole-wafer nanotip array mold, having billions of localized electrochemical reactions happen simultaneously, and transfer-printing nanoparticles on a one-to-one base. Unlike many other tip-based nanomanufacturing processes which require the mechanical contact between the nanotips and the substrates, this process is a non-contact, wearless transfer printing process, which only consumes the metallic coating on top of nanotips; therefore, one mold can be reused to create many devices by repeatedly recoating the nanotips with “metallic inks”. In addition, one coating of the nanotip mold is also able to print multiple devices continuously. Although only a nanoparticle array was demonstrated here, with the
established proof-of-concept, the 3D Nano-TEEP process is able to print any three-dimensional nanopattern with ultrahigh throughput. With the technical merits described above, the 3D Nano-TEEP process reported here is a significant advance from previous tip-based nanomanufacturing technologies, and readily translates various nanodevices into industrial mass production.

6.2 Mechanism of 3D Nano-TEEP process

Figure 6.1a illustrates the whole wafer electrochemical 3D nanoprinting process. The printing mold shown on the left side was fabricated by a monolithic nanomanufacturing process, called simultaneous plasma-enhanced reactive ion synthesis and etching (SPERISE) [7]. It is a lithographyless process that creates a pseudo-randomly distributed uniform nanotip array with controlled height, aspect ratio, and density. The mold is then coated with the “metallic ink”, in this case a 150-nm-thick layer of gold. The “paper” should be another conductive surface with relatively small roughness. The mold (anode) and “paper” (cathode) were brought very close to each other to form a thin electrolytic microcell (1 – 2 μm), and upon applying electrostatic potential the dome-like 3D nanostructures can be faithfully printed on the conductive “paper” with the localized nanotip-enhanced electrochemical “ink” transfer process. The nanodomes were formed here because the nanotips were placed on top of the “paper” stationarily; however, the nanotip “pens” can “write” any nanopatterns on the “paper” surface in a similar way as “dip-pen” lithography if the printing mold is attached to an electrically-controlled motor with pre-programmed motion path. Depending on the spatial resolution of the motor, the size of the nanopattern is completely tunable.

Here, we just use silicon mold, gold “ink” and ITO “paper” as an example to demonstrate this process. Actually, the mold, “ink”, and “paper” could be any other materials, as long as the
mold has nanotip array, and the “ink” and “paper” are conductive materials. The mold can also have a certain curvature and print nanopatterns on curved surfaces as long as the “paper” is conformal to the macroscale topology of the mold. Therefore, the Nano-TEEP potentially could be a versatile tip-based nanolithography process.

**Figure 6.1b** elaborates the mechanism of the Nano-TEEP process at the atomic level. A positive electrostatic potential is applied on the silicon nanotip mold coated with a thin layer of gold, and the ITO surface was grounded as the substrate to receive the printed pattern. Once the applied electrostatic potential reaches the redox potential of gold, the gold atoms start to be ionized and dissociate from surface. Under electrostatic field, the gold ions drift across the aqueous gap, associate with the electrons at the cathode, and redeposit on the ITO surface. The nanostructure formation process here is associated with a layer-by-layer addition of gold atoms, which is a typical bottom-up nanofabrication process. The intensity of the electrostatic field is determined by the distance between the mold and substrate \((E = \frac{V}{d})\). Therefore, since the mold is conically-shaped and the substrate is planar, the distance will change linearly from the valleys between nanocones to tips, and so will the electrical field. The closer the mold to the substrate, the greater the localized EF difference between the valley and tip regions; and the greater the localized EF, the higher the gold ionization and deposition rate. This means the Nano-TEEP process is a near field phenomenon and can be enhanced by bringing the mold and substrate closer to each other. The fast and slow accumulation of gold atoms right below the nanotip and nanovalley respectively causes the nanodome-like topology on the substrate surface, as well as the one-to-one correspondence between the nanotip and printed nanoparticles. The above proposed mechanism is supported by previously publications [8], [9].
Figure 6.1c shows a subarea of the patterned 4” mold and the corresponding transfer-printed surface. The length of each large and small square pattern is 1/16 inch (~1.6 mm) and 30 μm respectively. These lithographic patterns were preserved on the substrates after the transfer printing process. The transfer-printed smooth area shows light color and high transparency. In contrast, the transfer-printed nanostructured area shows dark color and low transparency. The variation in color is due not to the different thickness, but to the plasmonic absorption of incident light by the transfer-printed nanoparticle array (simulation needed). This result also indicated that the vast assembly of nanoscopic one-to-one nanoprinting events can result in the faithful transfer of mesoscopic and macroscopic patterns.

**Figure 6.1:** (a) Illustration of the full-wafer tip-based additive nanolithography process, called Nano-TEEP. (b) The detailed nanoscopic mechanism of the Nano-TEEP process at atomic level. (c) An exemplary nanotip mold diced out of the 4 inch wafer and the corresponding transfer-printed nanosurfaces. Two crosses are shown in the bottom subfigure, which indicates the nanotip-printed region (black) and conventionally-plated region (red).
6.3 Nanoscopic study of 3D Nano-TEEP process

To nanoscopically investigate the Nano-TEEP process, we first examined the silicon nanotip surface and the gold-coated nanomold surface with a scanning electron microscope. Figure 6.2a shows a representative silicon nanotip surface with both 30° tilted and cross-sectional SEM images. The nanotips were fabricated to be high aspect ratio and very pointed to ensure the strong localized EF around the tip area for the enhanced transfer rate. The cone-to-cone topology variation is very small, which guarantees the size uniformity of transfer-printed nanoparticles. The dashed square indicates a 1 μm × 1 μm area, and around 14 nanocones present in this region. Statistically 14/μm² is also the average nanocone density over the entire surface by checking a series of SEM images at different locations. The nanocone was then coated with a thin layer of gold (Fig. 6.2b). As reported previously [10], the coating follows the Stranski-Krastanov growth mode, which resulted in both a thin layer of continuous film and particle-like sidewall nanotextures. Lower aspect ratio nanocones can be coated uniformly [11]. We also consistently observed that the gold tended to accumulate on top of the nanocones, which is desirable for the one-to-one transfer printing. The FEM simulation results (Fig. 6.2c) show that the electrostatic field intensity around the tip area is significantly stronger than around the base area, especially in the region right above the nanotip. The localized strong EF is caused by the aforementioned distance-induced enhancement as well as the topology-induced enhancement by the sharp nanotip. The strong and highly directional EF distribution is the key for the faithful nanotip-to-nanoparticle transfer printing process.
Figure 6.2: 30° tilted and cross-sectional SEM images of a representative silicon nanotip mold (a) without coating and (b) with gold thin film coating. The film growth follows the Stranski-Krastanov mode resulting in both ultra-thin continuous film and particle-like nanotextures. The rectangular region in (a) shows a 1 μm × 1 μm area for nanotip density and distribution analysis. (c) FEM computational result of the localized electrostatic field distribution showing the enhanced and directional EF around the tip area.

Figures 6.3a and 6.3b are top view SEM images of the representative transfer-printed nanosurfaces taken from the dark and light color regions respectively as shown by the crosses in Fig. 6.1c. From the distinction in texture, it is obvious that the region printed by nanotip mold showed isolated, pseudo-random, particle-like nanoislands with average diameter around 180 nm, and in contrast the region transfer-printed from smooth mold surface had much finer grains and did not show isolated nanoislands. Typically, such fine nanotexture is considered as smooth as a mirror. We further statistically calculated the average density and center-to-center distance of the printed nanoparticles with SEM images taken at different locations of the substrate. As shown in the 1 μm × 1 μm rectangular region in Fig. 6.3a, the countable particles are around 14 and the average distance is around 300 nm, which match with the previously counted nanotip density and tip-to-tip distance. The extremely small nanoparticles/nanodots between the large ones are probably formed by the random nucleation of the gold atoms during the transfer and deposition
process; therefore, they are not considered in the calculation. The statistic results quantitatively confirmed that the Nano-TEEP process is a nanoscopic one-to-one, nanotip-to-nanoparticle 3-dimensional transfer printing process with high fidelity. In addition, if we look at the surprisingly sharp boundary of nanoparticles shown in Fig. 6.3a, the resolution of the 3D Nano-TEEP process can be as high as 10 nm to create such sub-10 nm narrow nanogaps.

The 3D topology of the transfer-printed nanosurfaces was further characterized with atomic force microscopy (AFM). A 1.5 μm × 1.5 μm region was scanned for the particle-like surface and smooth surface respectively as shown in Fig. 6.3c and 6.3d. It is apparent by the images that the surface developed by Nano-TEEP process using the nanotip array master yields nanodome-like 3D structures with larger size, height and lateral distance than those of the surface electrochemically plated using the planar silicon master. This notion is further supported by the corresponding cross-sectional profile images. The nanotip-printed surface shows much higher peaks and sharper valleys than the conventionally plated surface, with the corresponding average peak-to-valley distance of 30 nm and 10 nm respectively. Furthermore, the root mean square (RMS) roughness data suggests that the nanotip-printed surface is nearly three times rougher than the mirror-like plated surface. The above quantitative characterization results showed the 3D topological difference between the surfaces created by 3D Nano-TEEP and conventional plating processes, and also demonstrated the excellent fidelity of the tip-based nanolithography technique in creating nanoscale features with ultrahigh resolution.
Figure 6.3: (a) SEM image of the nanotip-printed surface showing isolated, pseudo-random, particle-like nanoislands. The rectangular region shows a 1 μm × 1 μm area for nanoparticle density and distribution analysis. (b) SEM image of the conventionally-plated surface showing fine grain (< 10 nm) nanotextures similar to the coating of a mirror. (c) AFM image and cross-sectional profiling of the nanotip-printed surface. (d) AFM image and cross-sectional profiling of the conventionally-plated surface. The surface developed by Nano-TEEP process yields nanodome-like 3D structures with high RMS roughness, while the surface created by planar silicon master shows small and flat peaks and valleys with low RMS roughness.

6.4 Dynamic transfer printing process

The electrochemical nanoprinting process starts when the applied DC bias goes beyond a threshold that is dependent on the topology of the nanotips and the thickness of the electrolytic microcell sandwiched between the mold and substrate. Although the variation of threshold exists,
the Nano-TEEP process generally happens when the applied DC bias is larger than 2.5V. To determine the threshold voltage, we performed a linear sweep voltammetry experiment. Instead of sweeping voltage, we found that sweeping current at a constant rate and measuring voltage change gave distinct indications of different phases of the transfer printing process. As shown in a representative I-V curve (Fig. 6.4), when the current is lower than 200 μA, the voltage-current curve was smooth and linear, indicating a simple ohmic load in between the anode and cathode. The ionic transport initiated slowly at about 200 μA, which was indicated by the slight oscillation of the voltage. The violent metal redox and transfer process occurred from 250 μA to 340 μA, which was indicated by the intense oscillation of the measured voltage. This process lasted for around 7.5 minutes. Afterwards the transfer process became stabilized and the voltage oscillation evidently decreased, which was possibly due to the metal ion concentration in the liquid reaching an equilibrium value. This process is highly repeatable and controllable. One can deterministically manipulate the voltage threshold by controlling the topology of the nanotip and the thickness of the aqueous microcells. With the calibrated voltage threshold and transfer rate relationship, the height and aspect ratio of the transfer-printed nanopatterns can also be precisely controlled with a pre-calculated processing time.
Figure 6.4: The dynamic transfer printing process reflected by voltage-current (red) and resistance-current (blue) curves. The amplitude of the voltage oscillation indicates the different phases of the transfer printing process.

6.5 Conclusion

Previously, people have shown single STM or AFM tip-based nanolithography or parallel tip-based nanolithography in a small area with a specially-designed AFM cantilever array. The 3D Nano-TEEP process demonstrated here is the very first groundbreaking work to show wafer-scale tip-based electrochemical nanolithography with billions of identical transfer printing processes happening in parallel. The nanotip “pens” used in this work were fabricated with a cost-effective, single-step process reported previously. Although only pseudo-random metallic nanotip-to-nanoparticle transfer printing was shown here, the proof-of-concept of high-fidelity, high-resolution additive nanomanufacturing was successfully established. With the nanotip mold attached to a CAD-driven, electrically-controlled motor, the Nano-TEEP process will be able to “write” any nanopatterns in a high-yield, high-throughput manner. In addition, with the
mechanism of highly-localized electrochemical transfer printing established here, the Nano-TEEP is a versatile process and can be implemented by nanotip array with any arrangement, periodicity, aspect ratio, and metallic coating of any type and fabricated with any previously demonstrated methods, such as nanosphere lithography, interference lithography, and EUV lithography.

We also demonstrated that the Nano-TEEP process operates in an ambient environment with a simple, low-cost electrochemistry experimental set-up, but can achieve nanofabrication capability beyond what complex and expensive clean-room equipment can deliver. Given its room-temperature operation, low voltage and energy requirement, and low environmental impact (localized electrochemical reaction constrained in the electrolytic microcell), the Nano-TEEP process is fully compatible with next-generation green nanomanufacturing.

6.6 References


