

**DEVELOPMENT AND CHARACTERIZATION OF HIGH
ASPECT RATIO NANOSTRUCTURES ON LARGE AREA OF
POLYSTYRENE SURFACE**

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DEPARTMENT OF MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

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DEPARTMENT OF MECHANICAL ENGINEERING

Submitted

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DEDICATED TO MY LOVING FAMILY

CERTIFICATE

This is to certify that the thesis entitled, “**Development and Characterization of High Aspect Ratio Nanostructures on Large Area of Polystyrene Surface**” submitted by **Mrs. Anagdha** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Mechanical Engineering is a bona fide record of original research work carried out by her under our supervision in conformity with the rules and regulations of the institute.

The results presented in this thesis have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.

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ABSTRACT

The prime focus of this research is to fabricate high aspect ratio nanostructures on large area of polystyrene surface so that they can be availed for actual practical application. Micro/nanostructures enhance several properties of the material due to increased surface area-to-volume ratio but the various ways of modifying the surface of the material offer resolution and cost limitations. Therefore, there is a need to develop a method for fabricating structures on a wider surface area. The surface morphology of polystyrene has been modified with different nanostructures by utilizing a method of hot embossing. This method assisted in large area coverage with nanofeatures.

A cost-effective and micron-resolution hot embossing set-up was developed. It is capable of patterning polymers as well as soft metals. High-temperature range, micron resolution movement of the stage at a desired speed, controlled motion of mould towards substrate and high load capacity are some of the salient features of indigenously developed machine. The developed set-up overcomes the limitations of available fabrication techniques which can make nanostructures to a very small area ($500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$). It is capable of fabricating structures on the area of $5\text{ cm} \times 10\text{ cm}$ with micron resolution which is otherwise not possible with available methods.

Different moulds with nanofeatures were prepared to obtain nanoholes and nanowires on the large area of polystyrene. DC electrodeposition was utilized to deposit nickel into the high aspect ratio holes of the alumina template and COMSOL 5.5 simulation was employed to understand the filling pattern during electrodeposition. A nickel shim with vertically standing nickel nanowires of diameter 400 nm and length $50\text{ }\mu\text{m} - 70\text{ }\mu\text{m}$ was produced after dissolving the anodized aluminium oxide (AAO) membrane which was then used as a mould to produce high aspect ratio nanoholes of average diameter 250 nm and length $20\text{ }\mu\text{m} - 30\text{ }\mu\text{m}$ on large

area of polystyrene. Shrinkage offered by polystyrene helped in reducing the diameter of the replicated nanoholes. Fabricated surface with nanoholes was further characterized for wettability and was found to exhibit a hydrophilic nature with a reduction of 56.2° in water droplet contact angle.

The physical vapour deposition method was utilized for filling up the pores of the AAO membrane with copper followed by sintering thereby producing a copper mould with nanowires of diameter 400 nm and length 5 μm . Nanoholes were replicated using this mould of nanowires. Hot embossing parameters were manipulated to obtain high shrinkage in the polystyrene thus creating nanoholes of very small diameter i.e., 25 nm to a maximum of 215 nm. The patterned surface was characterized by anti-reflectance and a reduction from 16.8% to 5.5% was observed in reflectance spectra.

The electroless method was also used to form a layer of nickel on each and every intricate detail of the AAO membrane thereby strengthening it to be used as a mould. When used for manipulating polystyrene surfaces at different hot embossing parameters, nanowires of polystyrene having unique shapes were produced. Flat tip nanowires of diameter 400 nm and length 30 μm - 50 μm and cup-shaped tip nanowires of average diameter 380 nm and length 40 μm - 60 μm were produced by carefully varying embossing load and temperature. Nanoparticles embedded cup-shaped tip nanowires were also produced by utilizing the same mould and further enhancement in surface area-to-volume ratio was observed due to uniform dispersion of nanoparticles through the polystyrene sheet. All kinds of nanowires produced were characterized for light entrapment and a decrease of reflectance from 16.8% to 8.8% (flat tip), 5.58% (cup-shaped tip) and 4.8% (nanoparticles embedded cup-shaped tip) was observed.

Keywords: Micro-nanostructured surfaces, Functional surfaces, Hot embossing, Large area, Polystyrene, Electrodeposition, Electroless plating, Anti-reflection, Hydrophilic

अभिषद

इस अनुसंधान का मुख्य ध्यान उच्च आकार अनुपात नैनो संरचनाओं की निर्माण है जो पॉलिस्टायरीन सतह के बड़े क्षेत्र पर लगाए जा सकते हैं ताकि वास्तविक व्यावसायिक उपयोग के लिए उपलब्ध हों। माइक्रो/नैनो संरचनाएँ सतह के विस्तार के कारण सामग्री की कई गुणों को बढ़ाती हैं, लेकिन सामग्री के सतह को संशोधित करने के विभिन्न तरीके समर्थन और लागत की सीमाएँ प्रदान करते हैं। इसलिए, एक व्यापक सतह के संरचनाओं का निर्माण करने के लिए एक विधि का विकास की आवश्यकता है। पॉलिस्टायरीन की सतह की सर्ववर्गी बदलती विविध नैनो संरचनाओं के साथ गरम छापाई के एक विधि का उपयोग किया गया है। यह विधि नैनो विशेषताओं के साथ बड़े क्षेत्र कवर करने में मदद करती है। एक लागत-कुशल और माइक्रॉन-संकल्पित गरम छापाई सेट-अप विकसित किया गया। यह पॉलिमरों को पैटर्निंग करने की क्षमता रखता है साथ ही नरम धातुओं को भी। उच्च तापमान सीमा, माइक्रोन रिज़ॉल्यूशन स्टेज की चाहिए गई गति पर, मोल्ड के प्रति तपेदिक की नियंत्रित गति और उच्च भार प्रतिभागिता कुछ अभिलक्षण विशेषताएँ हैं जो स्वदेशी रूप से विकसित मशीन की हैं। विकसित सेट-अप मौजूदा निर्माण तकनीकों की सीमाओं को पार करता है जो नैनो संरचनाओं को एक बहुत छोटे क्षेत्र ($500\ \mu\text{m} \times 500\ \mu\text{m}$) तक ले जा सकते हैं। यह उपलब्ध विधियों के साथ संभावित नहीं है। यह माइक्रोन रिज़ॉल्यूशन के साथ $5\ \text{सेमी} \times 10\ \text{सेमी}$ के क्षेत्र पर संरचनाएँ निर्मित करने की क्षमता रखता है जो अन्यथा संभव नहीं है। विभिन्न मोल्ड नैनो विशेषताओं के साथ तैयार किए गए थे ताकि पॉलिस्टायरीन के बड़े क्षेत्र पर नैनोहोल और नैनोवायर्स प्राप्त किए जा सकें। उच्च आकार अनुपात के छिद्रों में निकेल को जाल टेम्पलेट के अंदर जमाने के लिए डीसी इलेक्ट्रोडिपोजिशन का उपयोग किया गया और इलेक्ट्रोडिपोजिशन के दौरान भराई गई पैटर्न को समझने के लिए COMSOL 5.5 सिमुलेशन का उपयोग किया गया। एक निकेल शिम उत्तेजित अल्यूमिनियम ऑक्साइड (एएओ) मेम्ब्रेन की घोली को विघटन करने के बाद उत्पन्न किया गया था जो फिर पॉलिस्टायरीन के बड़े क्षेत्र पर औसत व्यास 250 नैनोमीटर

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List of Abbreviations

Abbreviation	Definition
1D, 2D, and 3D	One-dimensional, two-dimensional and three-dimensional
AAO	Anodized aluminium oxide
AC	Alternating current
AFM	Atomic force microscopy
ARS	Anti-reflective structures
CTE	Coefficient of thermal expansion
CVD	Chemical vapour deposition
DC	Direct current
DI	Deionized
DSC	Differential Scanning Calorimetry
EBL	Electron beam lithography
EDS	Electron dispersion spectra
FESEM	Field emission scanning electron microscopy
FIB	Focused ion beam
G'	Storage modulus
G''	Loss modulus
MEMs	Micro-electromechanical systems
NTSs	Nanotextured Surfaces

P2P	Plate-to-plate
PC	Polycarbonate
PDMS	Poly-dimethyl siloxane
P _E	Embossing pressure
PE	Polyethylene
PET	Polyethylene terephthalate
PMMA	Poly (methyl methacrylate)
PP	Polypropylene
PS	Polystyrene
PVD	Physical vapour deposition
R2P	Roll-to-plate
R2R	Roll-to-roll
RIE	Reactive ion etching
SEM	Scanning electron microscopy
SPR	Surface plasmon resonance
T _D	Demolding temperature
T _E	Embossing temperature
TEM	Transmission electron microscopy
T _g	Glass transition temperature
T _R	Room temperature
UV-VIS NIR	Ultraviolet-visible near infrared
WDCA	Water droplet contact angle