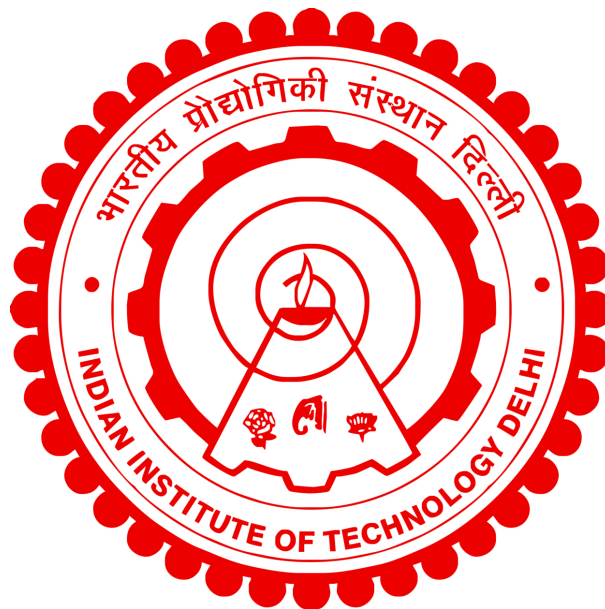


**INVESTIGATIONS INTO SOLID-STATE DEWETTING OF  
PLASMONIC MATERIALS ON PLAIN AND  
NANOSTRUCTURED SAPPHIRE SURFACES**

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MARCH 2025**

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NANOSTRUCTURED SAPPHIRE SURFACES

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*Submitted*

*In fulfillment of the requirements of the degree of*

Doctor of Philosophy

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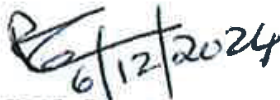
MARCH, 2025

*Dedicated to my parents and my wife,  
for their love, patience, and faith in me.*

# CERTIFICATE

This is to certify that the thesis titled **Investigations into Solid-state Dewetting of Plasmonic Materials on Plain and Nanostructured Sapphire Surfaces**, submitted by **Mr. Mahesh Yadav**, to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a bonafide record of the research work done by him under our supervision and guidance. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

  
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(Mahesh Yadav)

# ABSTRACT

Recently, substrate-supported noble metal nanostructures have attracted significant attention due to their plasmonic properties and applications in biosensing, photovoltaics, and optoelectronic devices. The plasmonic effects primarily depend on nanostructures material, size, shape, and spatial arrangement; therefore, controlling these aspects is essential. Fabrication of nanostructures by solid-state dewetting of thin metal films facilitates the cost-efficient solution over lithography-based methods. However, its large-scale implementation is limited by the inherent randomness in the resulting nanostructures. In order to gain control over the dimensional and form aspects of Au and Ag nanoparticles, this research study investigates the effect of film thickness and dewetting temperature. Moreover, mixing Au and Ag films resulted in the fabrication of monodispersed spherical alloyed (AuAg bimetallic) nanoparticles. In addition, it has facilitated linear tuning of their optical response in the visible range by varying Au:Ag thickness ratios.

When thermally annealed, the vicinal surfaces of sapphire undergo reconstructions to reveal periodic nanoscale step-terrace structures on their surfaces. In order to control the dimensions of such step-terrace structures, the effect of temperature on their morphology evolution is studied by multi-stage thermal annealing. It is shown that low-temperature annealing followed by high-temperature annealing in multiple stages resulted in the step-terrace structures with larger step heights.

The sapphire substrates with such nanoscale structures were then used to study their



effect on the solid-state dewetting of Au and Ag thin films to fabricate their ordered nanoparticles. It is observed that step-terrace structures with a step height comparable to the film thickness can induce spatial order in the resulting nanoparticles. The synergy between the two methods is achieved by combining two scalable and cost-effective processes, thermal annealing of sapphire substrates for fabricating periodic nanostructures on it and solid-state dewetting of thin metal films.

**Keywords:** Nanostructures, Plasmonic, Solid-state dewetting, Vicinal Sapphire, Thermal annealing, Step-terrace structures, Ordered nanoparticles

## अमूर्त

हाल ही में, सब्सट्रेट-समर्थित नोबल मेटल नैनोस्ट्रक्चर ने अपने प्लाज़्मोनिक गुणों और बायोसेंसिंग, फोटोवोल्टिक्स और ऑप्टोइलेक्ट्रॉनिक उपकरणों में अनुप्रयोगों के कारण महत्वपूर्ण ध्यान आकर्षित किया है। प्लाज़्मोनिक प्रभाव मुख्य रूप से नैनोस्ट्रक्चर की सामग्री, आकार, आकृति और स्थानिक व्यवस्था पर निर्भर करते हैं; इसलिए, इन पहलुओं को नियंत्रित करना आवश्यक है। पतली धातु की फिल्मों के सॉलिड-स्टेट डीवेटिंग द्वारा नैनोस्ट्रक्चर का निर्माण लिथोग्राफी-आधारित विधियों की तुलना में लागत-कुशल समाधान की सुविधा प्रदान करता है। हालांकि, इसके बड़े पैमाने पर कार्यान्वयन परिणामी नैनोस्ट्रक्चर में निहित यादृच्छिकता द्वारा सीमित है। Au और Ag नैनोकणों के आयामी और रूप पहलुओं पर नियंत्रण पाने के लिए, यह शोध अध्ययन फिल्म की मोटाई और डीवेटिंग तापमान के प्रभाव की जांच करता है।

जब तापीय रूप से एनील किया जाता है, तो नीलम की विसिनल सतहें पुनर्निर्माण से गुजरती हैं, जिससे उनकी सतहों पर आवधिक नैनोस्केल स्टेप-टेरेस संरचनाएँ दिखाई देती हैं। ऐसी स्टेप-टेरेस संरचनाओं के आयामों को नियंत्रित करने के लिए, उनके आकारिकी विकास पर तापमान के प्रभाव का अध्ययन बहु-चरणीय थर्मल एनीलिंग द्वारा किया जाता है। यह दिखाया गया है कि कई चरणों में उच्च तापमान एनीलिंग के बाद कम तापमान एनीलिंग के परिणामस्वरूप स्टेप-टेरेस संरचनाएँ बड़ी ऊँचाई वाली बन गईं।

इस तरह के नैनोस्केल संरचनाओं वाले नीलम सब्सट्रेट का उपयोग तब व्यवस्थित नैनोकणों के निर्माण के लिए Au और Ag पतली फिल्मों के ठोस-अवस्था डीवेटिंग पर उनके प्रभाव का अध्ययन करने के लिए किया गया था। यह देखा गया है कि फिल्म की मोटाई के बराबर एक कदम ऊँचाई के साथ स्टेप-टेरेस संरचनाएं परिणामी नैनोकणों में स्थानिक क्रम को प्रेरित कर सकती हैं। दो तरीकों के बीच तालमेल दो स्केलेबल और लागत प्रभावी प्रक्रियाओं, आवधिक नैनोस्ट्रक्चर के निर्माण के लिए नीलम सब्सट्रेट की थर्मल एनीलिंग और पतली धातु फिल्मों की ठोस-अवस्था डीवेटिंग के संयोजन से प्राप्त किया जाता है।

**कीवर्ड:** नैनोस्ट्रक्चर, प्लास्मोनिक, सॉलिड-स्टेट डीवेटिंग, विसिनल सैफायर, थर्मल एनीलिंग, स्टेप-टेरेस संरचनाएं, ऑर्डर किए गए नैनोकण

# Contents

|                                                                                                               |            |
|---------------------------------------------------------------------------------------------------------------|------------|
| <b>ACKNOWLEDGEMENTS</b>                                                                                       | <b>i</b>   |
| <b>ABSTRACT</b>                                                                                               | <b>iii</b> |
| <b>List of figures</b>                                                                                        | <b>x</b>   |
| <b>List of tables</b>                                                                                         | <b>xi</b>  |
| <b>1 Introduction</b>                                                                                         | <b>1</b>   |
| 1.1 Background . . . . .                                                                                      | 1          |
| 1.2 Applications of plasmonic metal nanostructures . . . . .                                                  | 2          |
| 1.3 Methods of fabricating substrate-supported metal nanostructures . . . . .                                 | 5          |
| 1.4 Introduction to solid-state dewetting of thin metal films . . . . .                                       | 7          |
| 1.5 Introduction to vicinal sapphire surfaces . . . . .                                                       | 10         |
| 1.6 Thesis outline . . . . .                                                                                  | 16         |
| <b>2 Literature review</b>                                                                                    | <b>17</b>  |
| 2.1 Introduction . . . . .                                                                                    | 17         |
| 2.2 Optical properties of noble metal nanostructures . . . . .                                                | 18         |
| 2.3 Solid-state dewetting of thin metal films and fabrication of substrate supported nanostructures . . . . . | 23         |
| 2.3.1 Manipulation of size, shape, and areal density of resulting nanoparticles . . . . .                     | 24         |
| 2.3.2 Reducing the size dispersion of dewetted nanoparticles . . . . .                                        | 27         |
| 2.3.3 Controlling the spatial arrangement of nanoparticles . . . . .                                          | 29         |
| 2.4 Vicinal sapphire surfaces and geometry of step-terrace structures . . . . .                               | 31         |
| 2.4.1 Surface morphology evolution of vicinal sapphire surface by thermal annealing . . . . .                 | 33         |

|          |                                                                                         |           |
|----------|-----------------------------------------------------------------------------------------|-----------|
| 2.5      | Research motivation . . . . .                                                           | 37        |
| 2.6      | Research objectives . . . . .                                                           | 38        |
| <b>3</b> | <b>Materials and Methods</b>                                                            | <b>39</b> |
| 3.1      | Thin film deposition and solid-state dewetting . . . . .                                | 39        |
| 3.2      | Thermal annealing of miscut sapphire substrates . . . . .                               | 40        |
| 3.3      | Characterization Techniques . . . . .                                                   | 41        |
| 3.3.1    | SEM imaging and analysis . . . . .                                                      | 41        |
| 3.3.2    | Ultra-violet (UV)-visible spectroscopy . . . . .                                        | 42        |
| 3.3.3    | Transmission electron microscopy (TEM) imaging and elemental analysis . . . . .         | 43        |
| 3.3.4    | Atomic Force Microscopy (AFM) . . . . .                                                 | 49        |
| 3.4      | Summary . . . . .                                                                       | 52        |
| <b>4</b> | <b>Solid-state dewetting of Au, Ag, and Au-Ag bilayer thin films on plain sapphire</b>  | <b>53</b> |
| 4.1      | Introduction . . . . .                                                                  | 53        |
| 4.2      | Experimental details . . . . .                                                          | 54        |
| 4.3      | Results and discussion . . . . .                                                        | 55        |
| 4.3.1    | Ultrathin films of Au and Ag in as-deposited condition . . . . .                        | 55        |
| 4.3.2    | Low-temperature annealing of Au and Ag ultrathin films . . . . .                        | 56        |
| 4.3.3    | High-temperature annealing of Au and Ag ultrathin films . . . . .                       | 62        |
| 4.3.4    | Thermal annealing of Au-Ag bilayer thin films . . . . .                                 | 73        |
| 4.3.5    | Optical response of AuAg bimetallic nanoparticles . . . . .                             | 84        |
| 4.4      | Summary . . . . .                                                                       | 89        |
| <b>5</b> | <b>Surface morphology evolution of miscut sapphire by multi-stage thermal annealing</b> | <b>90</b> |
| 5.1      | Introduction . . . . .                                                                  | 90        |
| 5.2      | Experimental details . . . . .                                                          | 91        |
| 5.3      | Results and Discussion . . . . .                                                        | 92        |
| 5.3.1    | Influence of dwell-time on the periodicity and the step height . . . . .                | 92        |
| 5.3.2    | Comparison of surface morphology of sample C and sample B . . . . .                     | 97        |
| 5.4      | Summary . . . . .                                                                       | 104       |

|          |                                                                                                                   |            |
|----------|-------------------------------------------------------------------------------------------------------------------|------------|
| <b>6</b> | <b>Solid-state dewetting of Au and Ag ultra-thin films on nanoscale step-terrace structured sapphire surfaces</b> | <b>106</b> |
| 6.1      | Introduction . . . . .                                                                                            | 106        |
| 6.2      | Experimental details . . . . .                                                                                    | 107        |
| 6.3      | Results and Discussion . . . . .                                                                                  | 107        |
| 6.3.1    | Solid-state dewetting of Au thin films on step-terrace structured sapphire . . . . .                              | 108        |
| 6.3.2    | Solid-state dewetting of Ag thin films on step-terrace structured sapphire substrates . . . . .                   | 113        |
| 6.3.3    | Optical response of Au and Ag nanoparticles on plain and step-terrace structured sapphire substrates . . . . .    | 117        |
| 6.4      | Summary . . . . .                                                                                                 | 119        |
| <b>7</b> | <b>Conclusions and future scope</b>                                                                               | <b>120</b> |
| 7.1      | Conclusions . . . . .                                                                                             | 120        |
| 7.2      | Future scope . . . . .                                                                                            | 122        |
|          | <b>References</b>                                                                                                 | <b>136</b> |
|          | <b>Brief biodata and publications</b>                                                                             | <b>137</b> |

## List of Figures

|     |                                                                                                                                              |    |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.1 | Applications of plasmonic metal nanostructures . . . . .                                                                                     | 3  |
| 1.2 | Applications of ordered plasmonic metal nanostructures . . . . .                                                                             | 5  |
| 1.3 | Schematic illustration of solid-state dewetting process of thin metal film deposited over the substrate . . . . .                            | 7  |
| 1.4 | Winterbottom construction describing the equilibrium shape of the solid island resting on the rigid substrate . . . . .                      | 8  |
| 1.5 | Surface morphology evolution of surfaces not represented on equilibrium crystal shape (ECS) . . . . .                                        | 12 |
| 1.6 | Crystal planes of sapphire and atomic arrangement in its unit cell . . . . .                                                                 | 13 |
| 2.1 | Schematic illustration of localized surface plasmon resonance (LSPR) . . .                                                                   | 19 |
| 2.2 | Effect of Au nanoparticle's shape on the dipole plasmon resonance. . . . .                                                                   | 21 |
| 2.3 | Schematic illustration of the grooving at the grain boundaries of the film leading to void nucleation. . . . .                               | 23 |
| 2.4 | Geometry of step-terrace structures on the vicinal C-plane sapphire surface                                                                  | 32 |
| 3.1 | Temperature-time profile (not to scale) of each stage during multi-stage thermal annealing process. . . . .                                  | 41 |
| 3.2 | Sample surface after depositing the protective layer of Pt (on left); and after trench milling on both sides of Pt layer (on right). . . . . | 44 |
| 3.3 | Through milling of the membrane . . . . .                                                                                                    | 45 |
| 3.4 | Micromanipulator with the sample membrane. . . . .                                                                                           | 46 |
| 3.5 | Schematic illustration of attaching the membrane from micromanipulator to the TEM grid post. . . . .                                         | 47 |
| 3.6 | TEM sample membrane attached to the TEM grid post . . . . .                                                                                  | 48 |
| 3.7 | HAADF detector arrangement in STEM mode . . . . .                                                                                            | 49 |
| 3.8 | Photographic images of (a) Sapphire substrate (b) Dual-beam FIB-SEM system. . . . .                                                          | 50 |

|      |                                                                                                                                                                                                                            |     |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 3.9  | Photographic images of (a) Furnace controller and UV-Vis spectrophotometer<br>(b) Tescan Magna ultra-high resolution FE-SEM . . . . .                                                                                      | 51  |
| 3.10 | Photographic images of atomic force microscope (on left) and Silicon tips for<br>AFM (on right). . . . .                                                                                                                   | 52  |
| 4.1  | Au and Ag thin films in as-deposited condition . . . . .                                                                                                                                                                   | 57  |
| 4.2  | Low-temperature annealing of Au thin films . . . . .                                                                                                                                                                       | 58  |
| 4.3  | Low-temperature annealing of Ag thin films . . . . .                                                                                                                                                                       | 60  |
| 4.4  | Morphology of Ag NPs ( $t = 5$ nm) fabricated at different temperatures . .                                                                                                                                                | 64  |
| 4.5  | Morphology of Ag NPs ( $t = 10$ nm) fabricated at different temperatures .                                                                                                                                                 | 65  |
| 4.6  | Morphology of Au NPs ( $t = 5$ nm) fabricated at different temperatures . .                                                                                                                                                | 67  |
| 4.7  | Morphology of Au NPs ( $t = 10$ nm) fabricated at different temperatures .                                                                                                                                                 | 68  |
| 4.8  | Morphology analysis of dewetted Ag and Au NPs ( $t = 5$ nm) . . . . .                                                                                                                                                      | 70  |
| 4.9  | Morphology analysis of dewetted Ag and Au NPs ( $t = 10$ nm) . . . . .                                                                                                                                                     | 71  |
| 4.10 | Morphology of low temperature annealed Au-Ag bilayer ( $t = 5$ nm) film . .                                                                                                                                                | 74  |
| 4.11 | Morphology of low temperature annealed Au-Ag bilayer ( $t = 10$ nm) film .                                                                                                                                                 | 76  |
| 4.12 | Morphology of Au-Ag bimetallic NPs at $500^{\circ}\text{C}$ . . . . .                                                                                                                                                      | 78  |
| 4.13 | Morphology of Au-Ag bimetallic NPs at $750^{\circ}\text{C}$ . . . . .                                                                                                                                                      | 80  |
| 4.14 | Morphology analysis of dewetted Au-Ag bimetallic NPs ( $t = 5$ nm) . . . .                                                                                                                                                 | 81  |
| 4.15 | Cross-sectional TEM imaging and EDS elemental map of AuAg alloyed NPs<br>fabricated at $500^{\circ}\text{C}$ . . . . .                                                                                                     | 83  |
| 4.16 | EDS spectra confirming the compositional fraction of individual element in<br>the alloyed NPs fabricated by thermal annealing of 5 nm Au-Ag bilayer (60:40)<br>film. . . . .                                               | 84  |
| 4.17 | The normalized extinction spectra of AuAg bimetallic nanoparticles fabri-<br>cated from the 5 nm bilayer films of different Au:Ag thickness ratios at (a)<br>$500^{\circ}\text{C}$ and (b) $750^{\circ}\text{C}$ . . . . . | 86  |
| 4.18 | Plot of dependence of the LSPR peak wavelengths on different Au:Ag thick-<br>ness ratios at $500^{\circ}\text{C}$ and $750^{\circ}\text{C}$ . . . . .                                                                      | 87  |
| 5.1  | Surface morphology of miscut C-plane sapphire before and after thermal an-<br>nealing for 3 hours . . . . .                                                                                                                | 93  |
| 5.2  | Average periodicity and step height during multi-stage thermal annealing of<br>miscut sapphire . . . . .                                                                                                                   | 95  |
| 5.3  | Periodicity distribution of step-terrace structures . . . . .                                                                                                                                                              | 98  |
| 5.4  | Surface morphology evolution of sample C . . . . .                                                                                                                                                                         | 100 |

|      |                                                                                                                                                                     |     |
|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.5  | AFM image showing the surface morphology of sample B after 30 hours of thermal annealing . . . . .                                                                  | 102 |
| 6.1  | Surface morphology of sample D after 10 hours of thermal annealing at 1200°C                                                                                        | 109 |
| 6.2  | Morphology of Au NPs dewetted on plain and nanostructured sapphire substrates . . . . .                                                                             | 110 |
| 6.3  | Box plots comparing the size distribution of Au NPs ( $t = 3$ nm) on different sapphire samples. . . . .                                                            | 111 |
| 6.4  | Morphology of Au nanoparticles fabricated on different sapphire substrates                                                                                          | 112 |
| 6.5  | Box plots comparing the mean diameter and size distribution of Au NPs on plain sapphire and sample C substrates. . . . .                                            | 113 |
| 6.6  | Morphology of Ag NPs dewetted on plain and nanostructured sapphire substrates . . . . .                                                                             | 114 |
| 6.7  | Box plots comparing the size distribution of Ag NPs ( $t = 3$ nm) on different sapphire samples. . . . .                                                            | 115 |
| 6.8  | Morphology of Ag NPs fabricated on plain and sample D sapphire substrates. Histograms of their size distributions are shown below corresponding SEM images. . . . . | 116 |
| 6.9  | Box plots comparing the mean diameter and size distribution of Ag NPs on plain sapphire and sample D substrates. . . . .                                            | 117 |
| 6.10 | Optical response of Au and Ag NPs ( $t = 3$ nm) fabricated on different step-terrace structured sapphire substrates. . . . .                                        | 118 |



## List of Tables

|     |                                                                                                             |     |
|-----|-------------------------------------------------------------------------------------------------------------|-----|
| 4.1 | Thicknesses of Au and Ag in the 5 nm bilayer film . . . . .                                                 | 54  |
| 4.2 | Thicknesses of Au and Ag in 10 nm bilayer film . . . . .                                                    | 54  |
| 5.1 | Annealing conditions for multi-stage thermal annealing of miscut sapphire                                   | 91  |
| 6.1 | Summary of average dimensions of step-terrace structures fabricated on different sapphire samples . . . . . | 108 |