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

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by

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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.

7/12/24

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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 ऊंचाई 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

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