Synthesis of Plasmonic Thin Film for Multi-Functional Photonic Applications

Thesis Submitted in Partial Fulfillment for
the Award of Degree

Doctor of Philosophy

By

Sobhan Hazra

SCHOOL OF MATERIALS SCIENCE AND TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY) VARANASI
VARANASI – 221005
INDIA

Roll No. - 20111522 **2025**

Chapter 7

7.1 Conclusions

My PhD thesis is primarily built upon three key findings that have significantly shaped my research progress;

1. Development of a cost-effective, scalable synthesis technique of Plasmonic thin film by utilizing solution processed ion-conducting oxide as initial material.

2. Development of a mechanically flexible Ag based transparent conductor and transparent heat reflector and its application as a self-bias plasmonic photodetector and heat reflecting coat for smart window applications.

3. Fabrication of a novel bimetallic Au-Ag transparent conducting thin film and used that new technique in diverse fields of solar cells, plasmonic photodetector and biosensors applications.

I have leveraged these three key findings for multiple applications in photonic technologies. The striking features of this thesis work are the improvement of transparency and electrical conductivity of plasmonic NPs based transparent conducting film as an alternative of ITO coated film. A brief discussion of these applications follows in the subsequent section-

Firstly, the thesis addresses the oxidation issue of the plasmonic thin films that arises in Ag-based plasmonic devices due to open air instability. Till now researchers basically focus on colloidal or composite synthesis route for the fabrication of Ag-plasmonic film, but all these techniques have critical issues related to atmospheric stability. To mitigate this, we have introduced a novel low cost where lithium titanate ($Li_4Ti_5O_{12}$), an ion-conducting oxide is used as the initial material. This ceramic contains light ions like Li^+ and this mobile ion can move through the crystal channel easily. By taking advantage of these mobile ions, we have chemically replaced Li^+ by Ag^+ inside the dielectric matrix to form a stable Ag-TiO_2 thin film. This new innovation helps to fabricate plasmonic thin film with much more stability, making it feasible for multi-functional photonic applications. Using Ag-TiO_2 thin film, I have successfully fabricated a narrowband plasmonic hot electron based photodetector in photoconductor geometry. Device shows a very good detectivity of 3.19×10^{11} Jones with conclusive evidence of hot electron generation from the plasmonic part. This approach shows a record detectivity of a plasmonic photodetector with a photoconductor geometry.

Secondly, the concept of low cost and scalable synthesis of Plasmonic thin film is extended further by depositing Ag based transparent conducting film on a flexible PET (plastic) substrate via low temperature synthesis route. Initially, I demonstrated the development of Ag nanostructured based flexible transparent conductor and its application as a self-biased plasmonic photodetector. Moreover, I used this film to fabricate a cost-effective flexible transparent heat reflector for energy-efficient smart window applications. The integration of an Ag-TiO_2 thin layer, derived from a solution-processed LTO precursor via ion exchange, facilitated lateral Ag growth, enabling a percolated Ag network at ultrathin thickness (~10 nm) of Ag film. The resulting Ag/Ag-TiO_2 thin film exhibited a low sheet resistance of ~50 Ω/sq with >70% transmittances in the visible range, making it a promising candidate for transparent electrode applications. This nanostructured Ag film is successfully employed in a plasmonic hot electron photodetector, leveraging its surface plasmon absorption to achieve a peak detectivity of 2.84×10^{12} Jones at 510 nm with a fast response time of ~25 ms. In parallel, the same Ag/Ag-TiO_2 bilayer structure is utilized to develop a flexible and environmentally stable THR coating, exhibiting high IR/NIR reflectivity (~85–90%) while maintaining 50–70% visible transmittance. A polymer overcoat (PMMA) further enhanced its durability. The effectiveness of this THR film is demonstrated in a real-world prototype, where its application on a glass window led to an internal temperature reduction of ~ 6–7°C under daylight conditions, underscoring its potential for smart window technologies.

Thirdly, I have extended these findings in the next level by developing a mechanically flexible and highly transparent bimetallic Au-Ag transparent conductor, which is comparable to commercially available ITO coated film. This work presents a scalable approach for fabricating highly transparent and conductive Au-Ag bimetallic nanostructures via PVD, utilizing a pre-deposited Ag-TiO_2/SnO_2 (or ZnO) NP seed layer with 4 nm Au deposition over it to induce percolated nano-porosity. The prepared film shows a sheet resistance of 5–10 Ω/□ and visible transmittance of 75–80%, enabling its application in plasmonic photodetectors, solar cells and biosensors. Film works as a transparent electrode as well as plasmonic hot electron generator in an M-S-M photodetector device configuration that achieves a peak detectivity of 1.6×10^{13} Jones at 750 nm with a fast response (~33 ms), demonstrating its efficacy for IR-sensitive optoelectronics. Additionally, its integration as a back electrode in inverted plasmonic organic solar cells (POSCs) yields record efficiencies of 7.8% (P3HT) and 11.17% (P3HT: $PC_{71}BM$) due to enhancement of open-circuit voltage in presence of plasmonic film, confirmed tandem cell formation. Furthermore, the porous Au-Ag nanostructured film serves as an ultrasensitive SERS substrate, detecting R6G and Vitamin B_{12} up to 1 pM & 1 nM, respectively. Overall, this study demonstrates the multi-functionality of Au-Ag nanostructures, offering a cost-effective and high-performance alternative for plasmonic optoelectronics, energy conversion, and molecular sensing applications.

7.2 Future Perspectives

The developed Ag and Au-Ag nanostructured films hold significant potential for advanced photonic applications beyond their current utilizations. Future research can be focused on optimizing their plasmonic properties for next-generation transparent photodetectors, extending their spectral sensitivity into the NIR and shortwave infrared (SWIR) regions for low-light imaging and night vision technologies. Additionally, their integration into ultrathin and flexible optoelectronic devices will be explored, including transparent touch sensors, wearable photodetectors, and smart windows with dynamic optical modulation. In energy applications, further engineering of these films could enhance light trapping in tandem and perovskite solar cells, improving energy conversion efficiency. Their unique SERS capabilities also make them promising for real-time biosensing and environmental monitoring, enabling label-free molecular detection with ultrahigh sensitivity. Furthermore, the nano-porous architecture of these films could facilitate surface plasmon-driven photocatalysis for sustainable chemical synthesis and pollutant degradation. The scalability and compatibility of these films with solution-processed techniques will also be explored for roll-to-roll fabrication, enabling cost-effective manufacturing of large-area photonic devices.

Overall, these advancements will position Ag and Au-Ag films as key materials for future photonic technologies spanning optoelectronics, energy harvesting, sensing, and environmental applications.