

PREFACE

Nanomaterials have drawn significant attention in recent years due to their numerous potential applications. These materials have been developed for various purposes, including improved chemical and colloidal stability, fabrication of photovoltaic devices and prevention of bacterial infection. Besides, tailoring the optical properties of nanomaterials, it's possible to apply different nanomaterials for various advanced photonic technologies. Particularly, thin films of metal nanoparticles have garnered significant attention in modern optoelectronics due to their ability to enhance light-matter interactions through localized surface plasmon resonance. These thin films, typically made from metal NPs like Ag, Au, and Cu are used to improve device efficiency in applications such as transparent conductors, solar cells, transparent heat reflectors, photodetectors, biosensors, and anti-bacterial coating. Their sensitivity to environmental changes makes them ideal for chemical and biological sensing, while their light-trapping capabilities enhance energy harvesting and photonic applications. As electronics continue to miniaturize and demand higher performance, plasmonic thin films offer a scalable, cost-effective solution with promising integration into next-generation technologies like quantum computing, wearable devices, and flexible electronics. With advancements in solution-based fabrication techniques, their future in energy-efficient systems, healthcare diagnostics, and photonics is particularly bright.

Researchers are increasingly interested in plasmonic thin film devices fabricated via solution-processed techniques because they offer a groundbreaking combination of cost and performance. The cost-effectiveness, scalability, and versatility, particularly suitable for large-area and flexible device applications. Solution processes such as spin-coating, dip-coating, and inkjet printing allow for the mass production of high-performance plasmonic devices without the need for expensive equipment or controlled environments, unlike sputtering, lithography techniques etc. Solution processing also allows seamless integration of plasmonic nanoparticles with other materials, enhancing their optical and electrical properties, thus paving the way for high-performance, low-cost devices in industries ranging from renewable energy to healthcare. As research continues, the ability to fabricate these

devices with precision and scalability is positioning solution-processed plasmonic thin films as a transformative technology in modern electronics.

To address the higher cost of these photonic technologies, we have introduced a novel cost-efficient technique where an ion-conducting metal oxide (ICMO) ceramic is used as initial material. This ceramic contains some light ions like Li^+ , Na^+ , K^+ etc. and these mobile ions can move through the crystal channel easily. By taking advantage of these mobile ions, we have chemically implanted conducting ions like Ag or Cu inside the dielectric matrix. This new innovation helps to fabricate plasmonic thin film with much more stability, making it feasible for multi-functional photonic applications. To utilize this phenomena, I have successfully fabricated an ion conducting dielectric $\text{Li}_4\text{Ti}_5\text{O}_{12}$ initially and then by doing surface chemistry we have developed an Ag- TiO_2 plasmonic thin film. Using Ag- TiO_2 thin film, I have successfully fabricated a narrowband plasmonic hot electron based photodetector in photoconductor geometry. Device shows a very high detectivity with conclusive evidence of hot electron generation from the plasmonic part.

Furthermore, by employing surface engineering with an ultra-thin plasmonic layer and Ag- TiO_2 thin film, I have successfully developed flexible transparent conductors, transparent heat reflectors, plasmonic solar cells, photodetectors, and active SERS substrates using a low temperature solution process and subsequent physical vapor deposition technique.

A concise overview of the subsequent thesis chapters is presented in the following section.

Chapter 1 provides a brief description of nanomaterials and their growing importance in modern technology. Owing to their unique stability, optical tunability, and multifunctional applications, nanomaterials have been widely explored in energy, healthcare, and photonics. In particular, thin films of metallic nanoparticles (Ag, Au, Cu) utilize localized surface plasmon resonance to enhance light–matter interactions, improving the performance of solar cells, sensors, transparent conductors, and antibacterial coatings. Their scalability, sensitivity, and light-harvesting capabilities make them highly promising for next-generation photonic, healthcare, and flexible electronic systems.

Chapter 2 provides a detailed synthesis process of a popular ion-conducting metal oxide dielectric $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), plasmonic Ag-TiO₂ thin film, semiconducting precursor solution like SnO₂, TiO₂, SnO₂ NPs, ZnO NPs, TiO₂ NPs, and preparation of polymeric solution like PMMA, P3HT, PC₇₁BM by solution process technique whereas devices are fabricated via spin coating and thermal evaporation technique. The detailed study of material and device characterization are explained in a very concise manner. The characterization techniques of XRD, UV-Visible, photo-luminescence, Raman, FE-SEM, AFM, HR-TEM, semiconductor parameter analyzer, EQE measurement unit along with reflectance and transmission measurement unit, etc. has been explained elaborately.

Chapter 3 discusses the development of Ag-TiO₂ thin film from an ion-conducting dielectric Lithium Titanium Oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) material via an in-situ growth technique and its application as a hot electron based plasmonic photodetector. The X-ray diffraction (XRD) measurement has been performed to confirm the phase of the material. UV-visible, and PL spectroscopy has been used to study the optical absorption and luminescence of active Ag-TiO₂ material. HR-SEM and HR-TEM has been performed to calculate the Ag NPs size and the composition of the material. This Ag-TiO₂ nano-Schottky junction has a low barrier height, high interface area with least interface state that enables efficient hot electron transfer to the conduction band (CB) of TiO₂, which is realized in the EQE data. This EQE data shows an intense photocurrent formation in the region of plasmonic absorption of Ag NPs, indicating the primary contribution of hot electrons on photocurrent production. This photodetector has been fabricated in a glass substrate in photoconductor geometry that shows a peak detectivity of 3.19×10^{11} Jones at 420 nm with a response time of ~ 2 sec.

Chapter 4 is separated into two sections; the first section discusses the development of Ag nanostructured based flexible transparent conductor and its application as a self-biased plasmonic photodetector and the second section focuses on the fabrication of a cost-effective Ag/Ag-TiO₂ flexible transparent heat reflector for energy-efficient smart window applications.

4.1 Flexible Transparent Conductors with a Percolated Ag Nanostructure and its Application as Efficient Self-Bias Plasmonic Photodetector

A percolated Ag nanostructured-based transparent conductor has been deposited by physical vapor deposition (PVD) technique where lateral growth of Ag has been enhanced by a pre-deposited Ag-TiO₂ thin film. This Ag-TiO₂ film has embedded Ag nanoparticles (NPs) within TiO₂ thin film which is grown in a low temperature (100°C) solution processed technique that includes Li₄Ti₅O₁₂ (LTO) thin film deposition by a sol-gel method followed by ion-exchange (Li⁺ → Ag⁺) process to yield an Ag-TiO₂ thin film. The percolated Ag network has appeared as soon film mass-thickness reaches close to 10 nm, resulting in an abrupt drop of electrical resistivity of the film. This percolated Ag nanostructured thin film (10 nm Ag/Ag-TiO₂/plastic) has resistivity of ~ 50 ohm/□ and an average visual transmittance of >70% up to 450 nm. In higher wavelength range, transparency gradually reduces, and it reaches to ~50% at 600 nm which is mostly due to the plasmon absorption of this film. By utilizing its combined optical transparency and surface plasmon absorption, this film has been used to develop plasmonic hot electron photodetectors where Ag-thin film works as transparent electrode as well as plasmon induced photo-excited hot electron generation. Device has been fabricated on a highly doped n type Si (n⁺-Si) with a metal-semiconductor-metal (M-S-M) device geometry. External quantum efficiency (EQE) data reveal that photocurrent of this device is mostly generated in the plasmonic absorption region with a peak detectivity of 2.84×10¹² Jones at 510 nm under -3V external bias. Besides, the device shows fast response with a response time of ~25 ms.

4.2 Cost Efficient Ag/Ag-TiO₂ Coating Based Flexible Transparent Heat Reflector for Energy-Saving Smart Window

This work has demonstrated a mass-producible and low-cost transparent heat reflector (THR) fabrication method on a flexible substrate by using a pre-deposited silver nanostructures thin film which is grown in two step deposition method. Initially, polycrystalline LTO thin film has been grown on a plastic substrate by a low temperature processed sol-gel technique. Afterword, mobile Li⁺ of LTO thin film has been replaced by Ag⁺ by an ion-exchange method to form Ag-TiO₂ thin film. In the second step, 10 nm Ag has been deposited on top of Ag-TiO₂ thin film by thermal evaporation. This bilayer THR has IR/NIR reflectivity of ~85-90% in combination with its visible transmittance of ~50-70%. For higher environmental stability of this THR, a polymer film (PMMA) has been coated on top of this

Ag/Ag-TiO₂ coating. To realize the practical application of this THR, a prototype box with one transparent glass window coated with this THR film has been developed and its internal temperature has been investigated during daytime. A reduction of internal temperature of ~6-7°C has been observed due to this THR coating w.r.t the reference uncoated box, indicating its plausibility as energy-saving smart window applications.

Chapter 5 is also categorized into two subparts; the first part discusses about the development of visible to IR active highly transparent Au-Ag bimetallic conducting film and its application as an efficient plasmonic photodetector on plastic substrate, and the next part I demonstrated an enhanced energy conversion plasmonic organic solar cell using this Au-Ag bimetallic transparent conducting film as a back electrode.

5.1. Visible to IR Active Highly Transparent Au-Ag Bimetallic Conducting Film and its Application as an Efficient Plasmonic Photodetector on Plastic Substrate

This section of this chapter demonstrated a gold (Au)-based transparent conductor by PVD technique where nano-porous of Au-Ag bimetallic nanostructured has been enhanced by a pre-deposited Ag-TiO₂/SnO₂ or ZnO NPs thin film. This Ag-TiO₂ thin film is an Ag NPs embedded TiO₂ thin film that has been grown over SnO₂ or ZnO NPs which leads to a percolated nano-porous-like structure. Prior to this, the surface morphology of the film shows a clear transition from spherical nanoparticles to percolated nano-porous Au-Ag bimetallic nanostructure with random hole formation that results in an abrupt jump of electrical conductivity when deposition reaches to 4 nm mass thickness of Au. This percolated nano-porous structure thin film (4 nm Au/Ag-TiO₂/SnO₂ or ZnO NPs /plastic) has a low resistivity of ~ 5-10 ohm/□ and an average visual transmittance around 75-80 % in the visible region. This film has been used to develop a metal-semiconductor-metal (M-S-M) plasmonic hot electron photodetector where Au-Ag thin film works as a photo-excited hot electron generation. External quantum efficiency (EQE) data reveal that photocurrent of this device is mostly generated in the plasmonic absorption region with a peak detectivity of 1.6×10^{13} Jones at 750 nm under -2V external bias. Besides, the device shows fast response with a response time of ~33 ms.

5.2. Au-Ag Bimetallic Transparent Conducting Thin Film for Boosting Energy Conversion Efficiency of Organic Solar Cell

Here, I discussed a new approach for enhancing the power conversion efficiency through an inverted plasmonic organic solar cells (POSCs) in a cost-effective way. As an alternative to ITO, I used our developed Au-Ag bimetallic transparent conducting film to back the electrode. A P3HT or a blended P3HT:PC₇₁BM organic polymer are used as an active material of this device whereas PEDOT: PSS and SnO₂ NPs are used as hole transport and electron transport layer respectively. The device with 120-140 nm thick active layer shows a remarkable power conversion efficiency of 7.8% for P3HT and 11.17% for blended P3HT:PC₇₁BM bulk heterojunction solar cells which are record efficiency with this materials combination that become possible due to enhancement of open circuit voltage by double, ensuring a tandem cell formation. This research offers a fresh, simple method to develop innovative plasmonic nanoparticles for enhancing the efficiency of OSCs.

Chapter 6 presents a straightforward method to fabricate a porous Au-Ag bimetallic nano-film on an inexpensive plastic substrate to detect SERS signal. Hollow and porous percolated nanostructures hold significant importance in SERS due to their intrinsic EM hotspots, multipolar resonance, and other factors. Au-Ag bimetallic film is fabricated via the same method as mentioned in the earlier chapter. This flexible substrate demonstrates effective SERS-based sensing, detecting Rhodamine 6G (R6G) dye and Vitamin B₁₂ down to 1 pM and 1 nM concentrations, respectively. The porous nature of the nano thin film aids in dispersing the analytes, thus lowering particle density for single molecule optical detection and enabling low-concentration measurements.

Chapter 7 summarizes the key outcomes presented in the thesis. Furthermore, the final part includes a brief outline of prospective research possibilities related to the current thesis.

List of journals and books used to bind up the thesis has been given at the end of the thesis as references