
Plasmonic Effect of Gold Nanoparticles (NPs) Surrounded by Multidielectric Matrices

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ABSTRACT

Plasmonic materials are the artificially manufactured materials (metamaterials) typically composed of nanostructure noble metals which give the unique optical properties superior to naturally occurring materials. Such plasmonic material has ability to give surface plasmon when electromagnetic light wave interact with free electrons in conduction band of the noble metals. Entirely absorption of light wave is the one of the major property of such plasmonic metamaterials. Recently, these metamaterials has drawn the attention of scientists because of its wide range of applications in harvesting energy and sensors. These applications are strongly dependent on adjusting the absorption band-width, peak position and absorption intensity. In this work we show that using ultra-thin multicomponent (i.e. Au NPs incorporated in mixture of SiO₂ and TiO₂ matrix) nanocomposite deposited on optically thick gold film through subsequent magnetron sputtering. Experimental results show that one can broaden the band-width and peak position to span Ultraviolet up to near infrared wavelength range.

Key Words:

1. INTRODUCTION

Nearly perfect absorption of electromagnetic light wave from range of visible to near-infrared frequencies is one of the recent most important properties of material which has broadened in its applications. From last year till to date, the developments to achieve perfect absorbers increased enormously because of its enormous interest in the development of material for solar energy for harvesting and sensors applications. With concern to the wide application range of perfect absorber, improved fabrication methods (such as perforated metallic films, grating structured systems, and metamaterials) have

also been taken into account till to date [1]. Out of different materials and composites which are limited by lack of stability, cost and also limited narrow absorbance spectral range, multi-component plasmonic nanocomposite where noble metal NPs (Nanoparticles) surrounded by dielectric matrices in the form of nanocomposites have gained significant research interest on experimental as well as theoretical basis due their variety of properties appropriate for various applications ranging from solar cells to biosensing devices. Furthermore, their absorbance spectra at broad range of frequencies could also be possible [1].

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The aim of this research work is to experimentally fabricate and characterize the optical properties of the three components super absorber structure. Another aim is to investigate perfect absorption behavior in wide frequency range. For this purposes, we use gold NPs (as a filler material) surrounded by TiO_2 and SiO_2 matrices (as dielectric environment). The absorption peak of depends on different materials parameters (such as dielectric environment, filling factor f and nanocomposite film thickness d). Increasing and decreasing refractive index (dielectric ratio) allow us to shift absorption peak from short to long wavelength ranges, respectively. Considering the index of refraction (material property), multicomponent (having different refractive indices) is used. The plasmonic properties of the nanocomposite films mainly determine by the type of noble metal (gold) NPs, their morphology and the dielectric constant of the embedding matrix. In dielectric constant, the refractive index of the matrices in nanocomposite plays a very important role in SPR (Surface Plasmon Resonance). Insulating matrices, such as SiO_2 , TiO_2 and polymers can be used to enhance the properties of plasmonic materials for different applications. The main reason behind the use of insulating matrices is to maintain necessary separation metallic NPs and also to avoid possible agglomeration of metallic NPs [2] and hence obtain an effective Plasmon resonance of metallic NPs and thereby SPP.

2. EXPERIMENTAL WORK

The physical vapor deposition of the gold film (on glass substrate) and entire nanocomposite (on 100 nm gold) were performed by a magnetron sputtering machine. **Fig. 1** shows the arrangement of functional layers on glass substrate.

Three magnetron targets (two RF sources and one DC source) can be run independently with rotatable sample

holder in order to achieve uniform distribution of the components and homogeneous film thickness. The schematic design of the magnetron sputtering process is shown in **Fig. 2**.

Based on the experimental results, it seems that the absorption efficiency of nanocomposite is mainly depends on three factors i.e. dielectric ratio, volume filling factor f and the nanocomposite film thickness d . The volume filling factor of the nanocomposite is estimated based on the rate of deposition. UV-Vis-NIR spectrometer (LAMBDA900-PerkinElmer) was used to collect the reflection (R) and transmission (T) of the samples and absorption (A) having no scattering, can be calculated



FIG. 1. SKETCH OF MAGNETRON SPUTTERING WITH THREE MAGNETRONS. SAMPLE IS PLACED UNDER THESE TARGETS AND ROTATING WITH CONSTANT SPEED

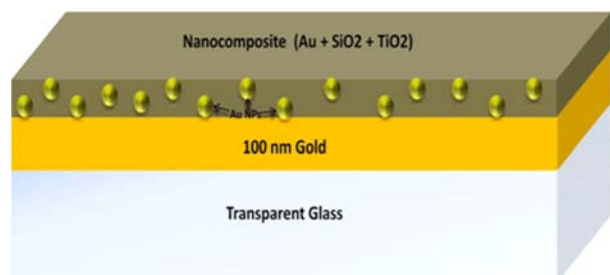


FIG. 2. SCHEMATIC OF THE GLASS SUBSTRATE COMPOSED OF THICK GOLD FILM AND NANOCOMPOSITE ON THE TOP

directly from transmittance (T) and reactance (R) using Kirchoff's rule ($A = 1 - T - R$). Film thickness and angle of refraction analysis of the samples were carried out with an automated angle M-2000® Ellipsometer (JAWoollam Co.). However, profilometry (Dektak XT-E-BRUKER) is also applied for gold film thickness measurements.

3. RESULTS AND DISCUSSION

Following previous work [1,3], it is known that the contribution of index of refraction may alter the absorption peak from short to long wavelength. Figure shows the absorption spectra of the nanocomposite deposited on optically thick gold film (100 nm Au film) with altered dielectric ratios ($SiO_2:TiO_2$). It is seen in Fig. 3 that by increasing the percentage of TiO_2 (having higher refractive index = 2.5) in nanocomposite, the absorption peak is shifting to longer wavelengths and its intensity going to drop. While by increasing the percentage of SiO_2 (having lower refractive index = 1.5), the absorption peak is shifting to shorter wavelengths. For higher percentage of TiO_2 (having higher refractive index) the retardation effect on

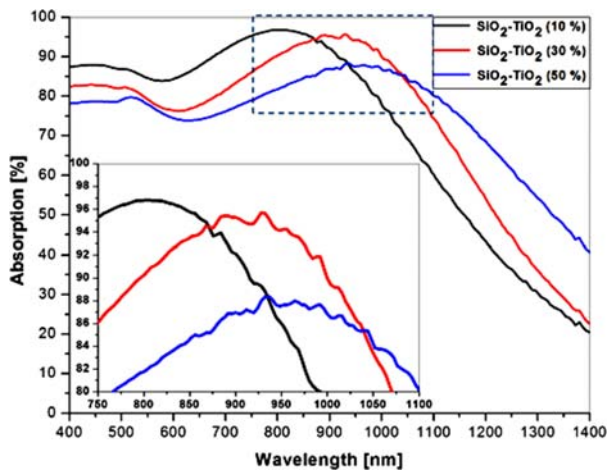


FIG. 3. UV-VIS ABSORPTION SPECTRA FOR NANOCOMPOSITE DEPOSITED ON THICK METALLIC FILM (100 NM AU FILM) WITH VARIOUS DIELECTRIC RATIOS 10% TiO_2 : 90% SiO_2 (BLACK CURVE), 30% TiO_2 : 70% SiO_2 (RED CURVE) AND 50% TiO_2 : 50% SiO_2 (BLUE CURVE) WHILE GOLD FILLING FACTOR (IE FF = 40%) AND NANOCOMPOSITE FILM THICKNESS (IE D = 50 NM) KEPT CONSTANT. INSET IS THE MAGNIFIED PLOT OF DASHED AREA

the resonance of the metallic particles is shifting the absorption band to a longer wavelengths [3]. While the absorption band to shorter wavelengths shift for higher percentage of SiO_2 is attributed to the higher resonance frequency for metallic particles in low dielectric medium is more dominant [1].

In order to maintain higher absorption intensity from VIS (Visible Information Statements) to NIR (Near-Infrared) frequency range, the dielectric matrices of SiO_2 as well as TiO_2 is adjusted at optimum ratio. From number of experiments, it is realized that 50% TiO_2 and 50% SiO_2 is the optimum condition for observing super absorption as shown in Fig. 3. If the percentage of TiO_2 will go beyond the optimum condition i.e. 50% of TiO_2 , one could not get perfect absorption (around 100%). From Fig. 3, one can see that at higher frequency the absorption for optimum condition (50% TiO_2 and 50% SiO_2) in nanocomposite is higher as compare to other dielectric ratios. This could be attribute to the greater percentage of dielectric constant (having high refractive index) in nanocomposite disturbs the condition of impedance matching to the vacuum and hence absorption decreases [1]. This is because of the contribution of high refractive index material is more in nanocomposite. Here the absorption dip is also very small and can be neglected. Hence the characteristic perfect absorption at effective dielectric ratios can also be seen from 400-1400 nm frequency in Fig. 3.

The microstructural morphologies of SiO_2-TiO_2 composites were investigated by TEM (Transmission Electron Microscopy) and are shown in Fig. 4. In Fig. 4 (Left), the bright field TEM image for nanocomposite where uniform distribution of SiO_2 and TiO_2 matrices in nanocomposite were observed, black and white spots correspond to the SiO_2 matrix and the TiO_2 matrix, respectively [4]. The SAED (Selected Area Electron Diffraction) patterns of nanocomposite film are shown right side of the bright-field TEM image. In Fig. 4 (Right), SAED pattern demonstrate that the TiO_2-SiO_2 matrices in the nanocomposite film are in an amorphous state.

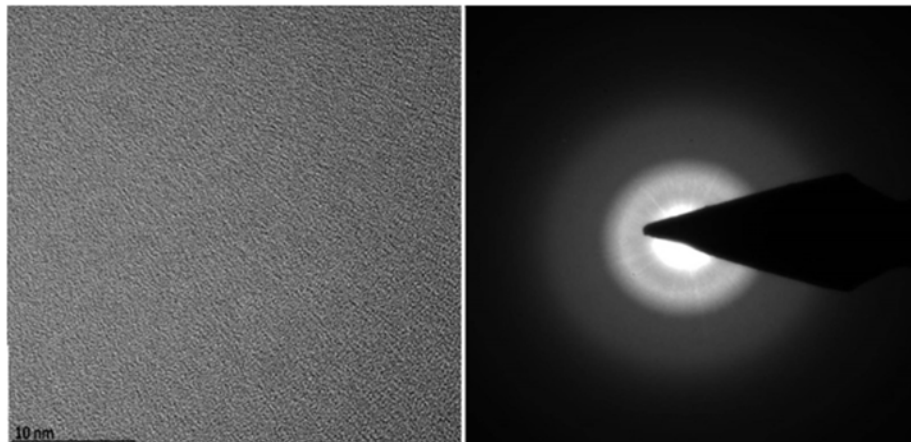


FIG. 4. BRIGHT-FIELD TEM IMAGE (LEFT) OF $\text{TiO}_2\text{-SiO}_2$ NANOCOMPOSITE. SiO_2 MATRIX CAN BE SEEN BY DARK WHILE TiO_2 MATRIX CAN BE SEEN BY BRIGHT AREA. THE SELECTED AREA ELECTRON DIFFRACTION (SAED) PATTERNS FOR THIN FILM NANOCOMPOSITE ARE SHOW ON RIGHT SIDE OF TEM IMAGE

4. CONCLUSION

We have fabricated a two functional layers perfect absorber by using a thick metallic film (100 nm gold film) and three components nanocomposite ($\text{SiO}_2\text{-Au-TiO}_2$). The fabrication technique is done by PVD magnetron sputtering. Adjusting dielectric ratio using different dielectric materials, we are able to tune our perfect absorber for wide range of wavelength spectrum.

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