www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2014.5745 Published online by the VBRI Press in 2015

Plasmonic resonance in spray deposited Au nanoparticles grown on TiO_2 thin film

Promod Kumar*, M. M. Ahmad

Functional Nanomaterials Research Laboratory, Department of Physics, National Institute of Technology, Hazratbal, Srinagar 190006, India

*Corresponding author. Tel: (+91) 194-2422032; E-mail: pkpmcm@gmail.com

Received: 19 November 2014, Revised: 13 March 2015 and Accepted: 14 March 2015

ABSTRACT

Gold nanoclusters embedded in titania (TiO_2) matrix were synthesized by thermal spray method followed by thermal annealing in an inert atmosphere. The effect of annealing temperature on the plasmonic response and optical properties of gold nanocluster in titanium dioxide matrices have been investigated by using UV-visible absorption spectroscopy. The surface plasmon resonance (SPR) at metal-dielectric interface for gold nanoparticles has been observed for as deposited samples at 561.8 nm which degrade as a function of post annealing temperature. Field emission scanning electron micrographs confirm the presence of spherical nanoparticles whose size increases with post annealing temperature. The plasmonic resonance of noble metals at nanoscale is fundamentally and technologically important for light trapping photovoltaic and other applications.

Keywords: Surface plasmon resonance; nanostructures; spray pyrolysis; optical properties; gold.

Introduction

The surface plasmons resonance (SPR) absorption in noble metals at nanoscale have attracted significant attention due to their unique physicochemical properties, functionalities and high-speed optical communications properties as compared to their bulk counterparts. One of the most important aspects at the nanoscale is that the noble metals like silver and gold exhibit strong absorption in visible range. The origin of this absorption is attributed due to their collective oscillation of conduction band electron in response to the electrical field of the electromagnetic radiation of light **[1-2]**. The SPR wavelength of plasmonic materials critically depends on the size, shape, inter-particle separation, volume fraction of the metal and the dielectric constant of the embedding matrix **[3-6]**. Plasmonic materials e.g. silicate glasses containing noble metal nanoclusters are exceptionally promising candidates for ultrafast optical switches and modulators. Glasses containing metal nanoclusters can be fabricated using methods such as ion implantations, thermal ion exchange, melt quenching and sol–gel processing etc. In general highly efficient nonlinear optical materials based devices are expected to become important for high-capacity communications networks in which the ultrafast switching signal regeneration and high capacity optical recording media is required. The roles of different matrices for plasmonic behaviour of metal nanoparticles have been studied by several researchers **[4-9]**. Titanium dioxide (TiO_2) is one of such most studied high resistive semiconducting oxide materials with a wide band gap (anatase: 3.2 eV; rutile: 3.0 eV) as a promising visible light photocatalyst and photovoltaics material **[2-11]**. Due to large electron–hole recombination on titania (TiO_2) particles it is practically difficult to use it as a photovoltaic material. So here Titanium dioxide (TiO_2) thin film was used as a matrix for the deposition of gold nanoparticles by simple thermal pyrolysis method. The fabrication of plasmonic metamaterials structure can be used to increase the absorption of light in semiconducting oxide based thin film, where the film structure exhibits the properties that usually not found in natural materials, such as negative refractive index of materials. There is a lack of literature on the size and matrix dependent plasmonic properties that could be useful in light trapping photovoltaics for inorganic semiconducting materials by simple and low cost fabrication techniques. Therefore a coherent study has been done here to investigate the plasmonic properties of Au nanoparticles based semiconducting titania (TiO_2) thin film. In this work the TiO_2 thin film was first deposited on glass substrate by thermal spray method and then gold nanoclusters were grown on the top of the TiO_2 film by simple thermal spray at same temperature.

Experimental

Material and methods

The preparation of plasmonic metamaterials based thin film was done by simple and low cost spray pyrolysis technique.

The schematic representation for the film deposition is shown in **Fig. 1.** The microscopic commercial soda lime glass slides (purchased from Marienfeld Group, made in Germany) with composition (in weight %) of 72.0% SiO_2, 14.0% Na_2O, 0.6% K_2O, 7.1% CaO, 4.0% MgO, 1.9% Al_2O_3, 0.1% Fe_2O_3, 0.3% SO_3) of 0.5 mm thickness were used after cleaning. The glass slides were first cleaned in a soap solution, then by distilled water and ultrasonication in acetone for an hour at 60^0C. Finally the glass slides were dried in an oven at 80^0C and after drying 3 to 4 pieces of glass slides were kept in a hot plate at 400^0C for spray coating of TiO_2 thin film. For all the deposition of titania thin film and gold nanoparticles the spray coating conditions were kept identical. The height of nozzle to substrate was 14 cm while the pressure of inlet carrier gas was set at a scale of 2 bars. An airbrush (Richpen 112B, Japan) with a nozzle diameter of 0.2 mm was set in single action mode for each cycle of deposition. Each time 1 ml of solution was used for spray coating with the break of one minute. The TiO_2 thin film was prepared by using titanium chloride 1.0 M solution in toluene as a precursor, which was purchased from Sigma Aldrich. 2 ml of this solution was dissolved in a beaker containing a mixture of 100 ml distilled water and 20 ml of toluene. The solution was stirred for 5 minutes in a magnetic stirrer at room temperature and then the ultrasonication was done for an hour at 60^0C before using it for spray coating. The solution was then sprayed for 5 times on preheated glass substrate at 400^0C with N_2 as a carrier gas. After deposition the titania films were continuously heated on the hot plate for thirty minutes resulting into the change in the colour of glass slide. The TiO_2 thin film prepared at this stage (after deposition at 400^0C) by spray pyrolysis are levelled as "TiO_2 spray coated" samples throughout the paper. After this the gold nanoparticles were deposited on these TiO_2 thin films by spraying for 5 times at 400^oC. The solution for the deposition of gold nanoparticles was prepared by dissolving gold chloride (0.09 gram) (purchased from Sigma Aldrich of 99.9% purity) in ethanol (40 ml). Before coating the ultrasonication of this solution was done for homogenous dispersion and uniform coating for an hour at 60^0C. After the deposition of the gold nanoparticles the films were kept for constant heating for 4h in the same hot plate at 400^0C and then the films were allowed to cool naturally up to room temperature resulting into the mixture of light pink-green-gold colours thin films. The gold coated TiO_2 thin films prepared at this stage (after deposition at 400^0C and constant heating for 4h) by spray pyrolysis are levelled as "Au- TiO_2 spray coated" samples.

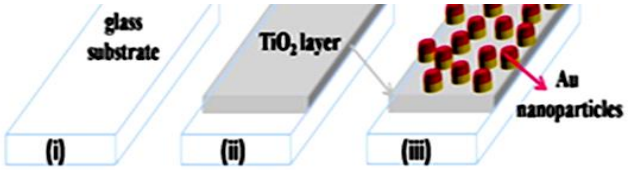

Fig. 1. Schematic of thin film grown by spray pyrolysis method for Au-TiO_2 film deposition.

To promote the formation of TiO_2, gold coated TiO_2 films and gold nanoclusters the thermal annealing of the samples in electrical tubular furnace at 600^0C for two hour has been carried out in the presence of N_2 gas atmosphere. To see the annealing effect on absorption properties of gold nanoparticles in titania matrix all the characterizations were repeated again. The TiO_2, gold coated TiO_2 annealed samples (after annealing at 600^0C for 2h in inert atmosphere) are levelled as "TiO_2 spray coated and annealed" and "Au- TiO_2 spray coated and annealed" samples respectively. Beside this, for comparison pure gold nanoparticles were deposited on glass substrate but it does not adhere to the glass surface and show similar morphology as observed after deposition on tirania thin films. All the experiments and characterizations at different stage were repeated 4-5 times for the reproduction and veracity of the work. The gold nanoparticles formation on TiO_2 thin film have been studied by Field Emission Scanning Electron Microscope (FESEM), UV Visible (UV-VIS) spectroscopy, Raman spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR) measurements to understand the growth mechanism, electronic, optical, and plasmonic properties during deposition and thermal annealing in N_2 atmosphere. The film thickness was measured by using the FESEM cross-sectional area image of the thin film. The Platinum (Pt) coating was done to make the surface conducting in all the samples, therefore a peak corresponding to Pt was observed in the EDX spectra.

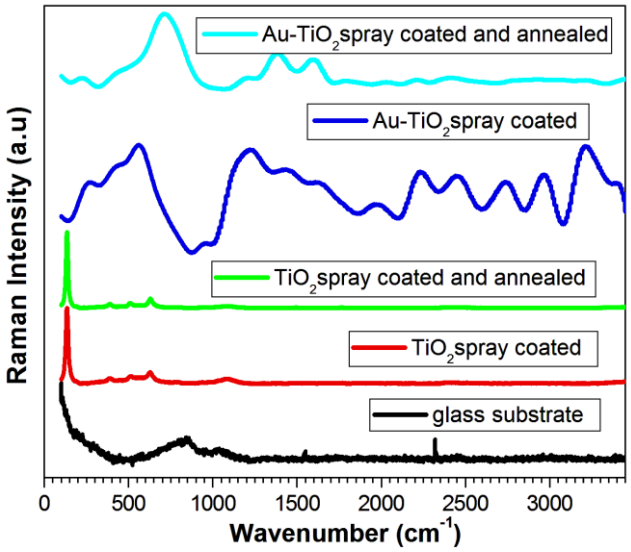

Fig. 2. Raman spectra of the glass substrate; TiO_2 spray coated; TiO_2 spray coated and annealed; Au-TiO_2 spray coated; Au-TiO_2 spray coated and annealed samples.

Results and discussion

Raman spectrum

Raman spectroscopy is a versatile tool for studying the structural, optical, atomic structure and electronic properties of multiphase semiconducting, hybrid materials and other layered graphene based semiconducting composites nanomaterials **[11]**. **Fig. 2** show the Raman spectra of glass substrate; TiO_2 spray coated; TiO_2 spray coated and annealed; Au- TiO_2 spray coated; and Au- TiO_2 spray coated and annealed samples. All the peak positions corresponding to various Raman bands of anatase phase in

TiO_2 spray coated and annealed sample has been assigned Eg, B1g, and A1g + B1g, for six allowed modes **[10-11]**. In case of Au- TiO_2 spray coated and annealed samples the anatase TiO_2 peak positions are missing and the new additional bands have been observed. These additional peaks position for Au- TiO_2 spray coated and annealed samples are mentioned clearly in **Table 1**.

Table 1. The main peak positions for various Raman bands observed in case of all samples.

Sample name *versus* band position	Band position in cm^{-1}
Pure glass	100, 840, 1030, 2320 cm^{-1}
TiO_2 spray	135, 390, 508, 630, 1060 cm^{-1}
TiO_2 spray and annealed	134, 385, 507, 630, 1060 cm^{-1}
Au-TiO_2 spray	258, 421, 562, 937, 1210, 1430, 1650, 1960, 2230, 2450, 2740, 2970, 3210 cm^{-1}
Au-TiO_2 spray and annealed	223, 429, 708, 1190, 1380, 1600, 1800, 2210, 2420 cm^{-1}

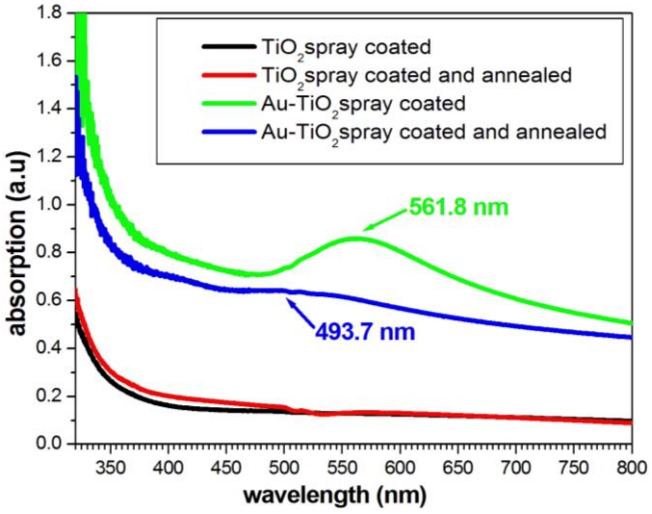

Fig. 3. Ultra violet-visible (UV-Vis) absorption spectra of the TiO_2 spray coated; TiO_2 spray coated and annealed; Au-TiO_2 spray coated; Au-TiO_2 spray coated and annealed samples.

Raman bands of pure anatase phase in Au- TiO_2 spray coated and annealed samples may be absent due to multiphase (existence of different mixed phases) nanostructures of metamaterials, different particle size distribution, shape distribution, morphological variations, discrepancy from stoichiometry as well as type of defects that contributes to the changes in the peak position, line width and shape of the mode in the Raman spectrum **[3, 11]**. It is noticeable that there is no background signal of the glass substrate in all the samples as it depends on the type of deposited material which shows the additional observed bands are due to Raman scattering of gold nanoparticles embedded in titania matrix, reveals the bonding differences between gold embedded titania matrices and presence of various functional group on the surface of the samples. After annealing the Au- TiO_2 spray coated sample the absence of few additional Raman bands (as observed in Au- TiO_2 spray sample) is observed clearly which is attributed to the removal of various functional groups present on the surface of the samples. Therefore, the exact interpretation of Au- TiO_2 spray coated and its annealed samples spectra in practice seems to be difficult due to the lack of literature in this particular technique of synthesis. An approach for solving this problem may be proposed separately in our future work.

UV-Vis spectroscopy

The absorption spectra for all the samples have been plotted in **Fig. 3**. The pure anatase TiO_2 has an indirect band gap of 3.1 eV (as calculated from Tauc plots of the indirect energy band gap) is due to transition from O 2p level in the valence band (VB) to Ti 3d energy states of conduction band (CB) **[3]**. The formation of gold nanoparticles is confirmed by the observation of the optical spectrum of their localized surface plasmon resonance absorption with a maximum at λ = 561.8 nm for Au- TiO_2 spray coated sample. The localized surface plasmon resonance (LSPR) for TiO_2 (semiconductor)-gold (metal) interface after annealing takes place at 493.7 nm for Au-TiO_2 spray coated sample exhibits a blue shift with poor absorption intensity.

The intensity of the SPR resonance decreases drastically after annealing in N_2 atmosphere is attributed to increase in the particle sizes of gold nanoparticles. Therefore the annealing after embedding plasmonic gold nanoparticles with TiO_2 resulting into the change in the refractive index of the surrounding medium. Therefore the observed decrease in intensity and blue-shift of the LSPR reduces effective refractive index of the matrix associated with pore formation, lower value of full width at half maxima (FWHM) with the increase in particle/cluster size, and removal of functional group present on the surface of the sample **[8]**. For a small clusters ($R \leq 10$ nm), this kind of decrease in FWHM with increase in clusters size is due to the mean free path effect of electrons **[4-6, 12]**. Au coated TiO_2 thin film gives an advance plasmonic metamaterial based semiconducting thin film which may be useful for superior light trapping low-cost photovoltaics and other optoelectronic applications. The UV-Vis absorption spectra of Au coated TiO_2 samples shows the gold nanoparticles of average size of 8 nm. The average size of Au nanoclusters was calculated by using formula given as follows in equation (1) **[4-6, 13-15]**

$$d = 2\frac{\hbar v_F}{\Delta E} \quad (1)$$

where d is the average cluster size of the nanoparticles, V_f = 1.39 × 10^6 m/s is the Fermi velocity of electrons in bulk gold and silver and $\Delta E_{1/2}$ is the FWHM of the SPR band. Equation **(1)** is valid as long the size of gold clusters is much smaller than the mean free path of the electrons in the bulk metal. The mean free path of the electrons is about 27 nm at room temperature for bulk silver and 20 nm for bulk gold **[14-15]**. To test the stability of plasmonic behaviour of these coated gold nanoparticles, UV-Vis absorption spectra of the films were collected after a period of one month which shows the similar absorbance behaviour of thin films with time indicates that gold nanoparticles are stable within that time frame.

Fourier transform infrared (FTIR) spectrum

The FTIR spectra for the entire sample were recorded in a range of 500 cm^{-1} to 4000 cm^{-1} as shown in **Fig. 4**. All the

peak, dip positions and different modes of vibration are mentioned in **Table 2**. The FTIR spectrum for few samples show a slope base line and an intense dip situated around a region of about 2320 cm^{-1} owing to the equipment background. This dip intensity is very low for few samples indicate a good adherence of TiO_2 film with the glass substrate.

Table 2. The main peak and dip positions for various bond stretching modes observed in FTIR spectrum.

Sample name versus bond position	Bond position in cm^{-1}
Pure glass	2270, 2330, 2450 cm^{-1}
TiO_2 spray	560, 1910, 2110, 2340 cm^{-1}
TiO_2 spray and annealed	1870, 2110 cm^{-1}
Au-TiO_2 spray	721, 1350, 1280, 1430, 1500, 1580, 1650, 1740, 1820, 1930, 2110 cm^{-1}
Au-TiO_2 spray and annealed	1490, 1650, 1730, 1820, 1930, 1970, 2090 cm^{-1}

The dip intensities corresponding to hydroxyl groups in all samples is very small implying that a large fraction of the O–H groups was removed during thermal spray reactions, while small content of vibrational bands such as C–H and C–O bonds are observed in the Au- TiO_2 spray coated sample, which reduces after annealing of the samples in inert atmosphere **[13-15]**. The presence of Si–O–Si, Si-O weak bands regions corresponding to bending or stretching mode of glass substrate are observed in few samples only, which indicate that most of the thin film are not transparent and they are strongly bonded with the glass substrate.

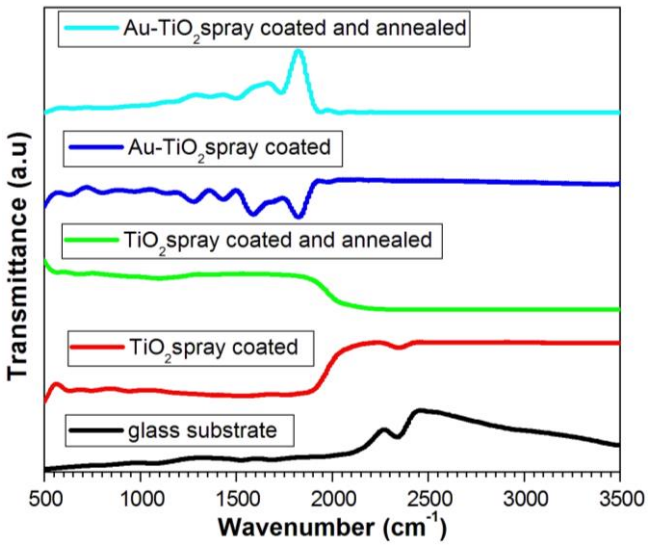

Fig. 4. FTIR spectra of the glass substrate; TiO_2 spray coated; TiO_2 spray coated and annealed; Au-TiO_2 spray coated; Au-TiO_2 spray coated and annealed samples.

Field emission scanning electron microscopy (FESEM)

To know about the growth processes and the morphological changes of without annealed and annealed TiO_2 and Au-TiO_2 spray coated samples during the film formation the thin film were characterized at different stage by field emission scanning electron microscopy (FESEM) at different magnification as shown in **Fig. 5.** The micrographs indicate that the TiO_2 thin film has cavities like honeycomb structure which is bonded to the glass substrate.

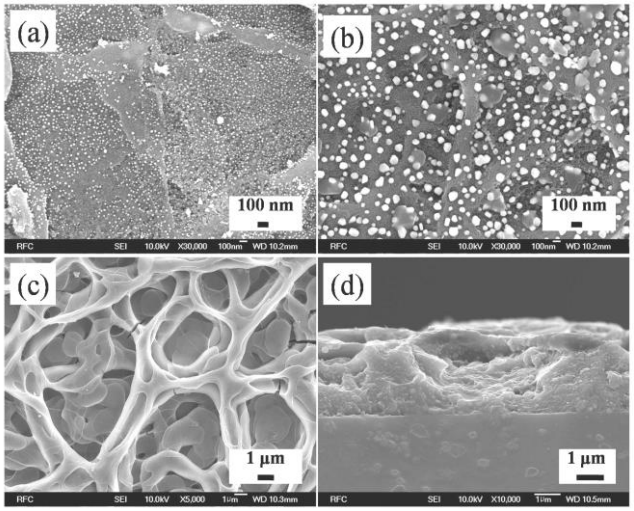

Fig. 5. Field emission scanning electron micrographs(FESEM) of (a) Au-TiO_2 spray coated at the 100 nm scale, (b) Au-TiO_2 spray coated and annealed samples at the 100 nm scale, (c) TiO_2 spray coated at 400°C at the 1 µm scale and (d) crosssectional micrographs of TiO_2 spray coated at 400°C at the 1 µm scale.

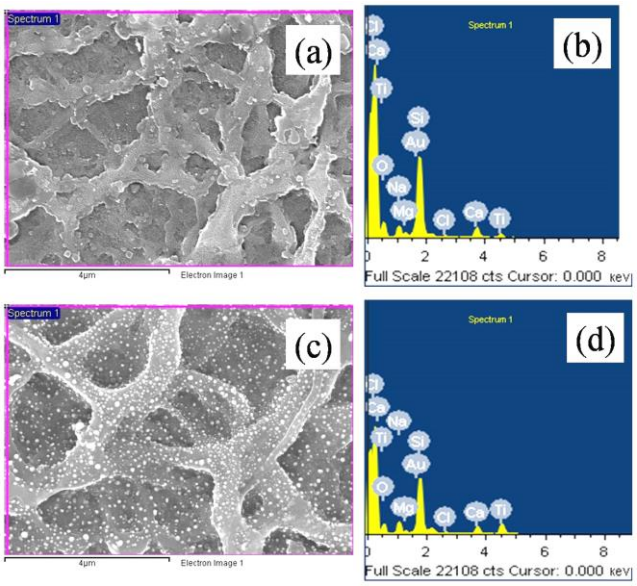

Fig. 6. (a) FESEM micrograph area selected for EDX pattern of Au-TiO_2 spray coated film; (b) EDX pattern of Au-TiO_2 spray coated film; (c) FESEM micrograph area selected for EDX pattern of Au-TiO_2 spray coated annealed film; (d) EDX pattern of Au-TiO_2 spray coated annealed film.

Upon subsequent deposition of Au nanoparticles on the TiO_2 film the gold nanoparticles get embedded inside the TiO_2 nanostructures, thus film work as an active adsorptive center for the deposition of Au nanoparticles. It is clearly seen that the gold nanoparticles are homogenously well attached on the surface of as-deposited TiO_2 thin film as shown in **Fig. 5** (a) and (b). The **Fig. 5**(c) shows the morphology for anatase TiO_2 thin film shows a similar morphology as reported previously **[11]**. It is clearly observed that the sizes of Au nanoparticles grown on the

TiO_2 matrix increases after annealing (the white particles in micrographs). The size of gold NPs in was measured individually from each FESEM image. The particle shape was nearly spherical for the nanoparticles of all sizes. At least 60 nanoparticles were counted for each sample to estimate the mean diameter and the relative standard deviation of the gold nanoparticles. The average Au particle size before annealing in TiO_2 is 34 nm which increases on an average up to 95 nm after annealing at 600^{o}C in inert atmosphere. The results are not consistent with UV-absorption results as there is a blue shift with reduced absorption intensity after annealing the Au- spray coated thin film. This inconsistency is attributed to random shape and size of the Au nanoparticles. This illustrates the fact that for gold plasmonic absorbance the particle size should be quite small **[11-15]**. The thickness of the film was measured about to 980 nm from cross-sectional micrographs as shown in **Fig. 5**(d). To verify the presence of all elements, Energy-dispersive X-ray spectroscopy (EDX) pattern for Au- spray coated thin films and annealed films were recorded and are shown in **Fig. 6.** The presence of all elements corresponding to Au, Ti, O and the glass substrate are confirmed from EDX pattern. The chlorine impurity has been identified on the surface of all the samples which does not play major role here for plasmonic behaviour of gold nanoparticles.

Conclusion

In conclusion, plasmonic metamaterials based Au in TiO_2 matrix based thin film was obtained by simple thermal spray pyrolysis method. This leads to plasmon resonance of gold nanoparticles at 561.8 nm. The annealing affect the plasmonic behavior of gold coated TiO_2 and exhibit a blue shift. The results suggest that the gold embedding in TiO_2 film by thermal spray does not change the band gap of TiO_2 while it useful for trapping of light in visible range. Thus the bonding of Au embedded TiO_2 thin film can significantly trap the light of a particular wavelength by mean of plasmonic resonance as well as increase the separation of photo- generated carriers for superior photovoltaic and optoelectronic applications.

Acknowledgements

The authors are highly thankful to Prof. (Dr) Rajat Gupta (Director NIT Srinagar) for taking keen interest in research and extending financial support for carrying out the research work. One of the authors, Promod Kumar, is also thankful to Shri Piyare Lal Saproo (PA to Director) of NIT, Srinagar for his generous help and support in administrative understandings. Promod Kumar is thankful to Dr. Arvind Agarwal and Mr. Mohan Chandra Mathpal of MNNIT, Allahabad, India for their kind support and valuable discussions for carrying out the research work.

Reference

1. U. Kreibig, M. Vollmer, Optical Properties of Metal Clusters, Springer, Berlin, **1995**.
2. M. C. Mathpal, A. K. Tripathi, M. K. Singh, S. P. Gairola, S. N. Pandey, *A. Agarwal. Chemical Physics Letters* **2013**, *555*, 182. **DOI:** 10.1016/j.cplett.2012.10.082
3. K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B 107*, **2003**, 668. **DOI:** 10.1021/jp026731y
4. Promod Kumar**,** Mohan Chandra Mathpal, Anand Kumar Tripathi, Jai Prakash, Arvind Agarwal, M. M. Ahmad and H. C. Swart, Phys. Chem. Chem. Phys. **2015** **DOI:** 10.1039/c4cp05679e
5. Promod Kumar**,** M. M. Ahmad, *Adv. Mater. Lett*. **2015**, *6(3)*, 242. **DOI:** 10.5185/amlett.2015.5634
6. Mohan Chandra Mathpal, Promod Kumar,Sachin Kumar, Anand Kumar Tripathi, Manish Kumar Singh, Jai Prakash and Arvind Agarwal, *RSC Adv*., **2015**, *5*, 12555 **DOI:** 10.1039/c4ra14061c
7. R. Philipp, G. R. Kumar, N. Sandhyarani, and T. Pradeep, *Phys. Rev. B* **2000**, *62*, 13160. **DOI:** 10.1103/PhysRevB.62.13160
8. H. Jia.; J. Zeng.; W. Song.; J. An.;B. Zhao, *Thin Solid Films 496*, **2006**, 281. **DOI:** 10.1016/j.tsf.2005.08.359
9. F. Ren, C. Jiang, C. Liu, D. Fu,Y. Shi, *Solid State Communication 135*, **2005**, 268. **DOI:** 10.1016/j.ssc.2005.04.013.
10. K. Tripathi, M. C. Mathpal, P. Kumar, M. K. Singh, S. K. Mishra, R. K. Srivastava, J. S. Chung, G. Verma, M. M. Ahmad, A. Agarwal. *Materials Science in Semiconductor Processing* **2014**, *23*, 136. **DOI:** 10.1016/j.mssp.2014.02.041
11. M. C. Mathpal, P. Kumar, Balasubramaniyan. R, J. S. Chung, A. K. Tripathi, M. K. Singh, M. M. Ahmad, S. N. Pandey, A. Agarwal. *Materials Letters 128*, **2014**, 306. **DOI:** 10.1016/j.matlet.2014.04.169
12. P. Manikandan , D. Manikandan , E. Manikandan , A. Christy Ferdinand, *Plasmonics*, **DOI:** 10.1007/s11468-014-9675-6
13. Jiawei Sheng, *International Journal of Hydrogen Energy 32*, **2007**, 2602. **DOI:** 10.1016/j.ijhydene.2006.10.007
14. B. Karthikenyan, *J. Appl. Phys*. **2008**, *103*, 114313. **DOI:** 10.1063/1.2936879
15. M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafigullin,.I. Vezmar, R. L. Whetten. *J. Phys. Chem*. B, **1997**, *101*, 3706. **DOI:** 10.1021/jp962922n