

# Effect of Silver Plasmonic Layer on $\text{Cu}_2\text{O}/\text{In}_2\text{S}_3$ Solar Cell

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**Abstract:** Solar cell with the structure  $\text{Cu}/\text{Cu}_2\text{O}/\text{In}_2\text{S}_3/\text{Ag@NP}/\text{Ag}$  was fabricated where the  $\text{In}_2\text{S}_3$  window layer and the plasmonic Ag nano particle thin film layer were deposited using injection chemical spray pyrolysis technique. Quantum efficiency measurement of these solar cells showed improved performance in the blue region of the visible spectrum compared to their counterparts. The films with Ag nano particles exhibited surface plasmon resonance peak at 432 nm which could be assigned to plasmon resonance of Ag nano-particles. The open circuit voltage of the best solar cell is 0.65 V, with short circuit current density of 1.2  $\text{mA}/\text{cm}^2$ , fill factor 22% and efficiency 0.17 %. We conclude that the in-coupling of light by the metallic nanoparticle thin film layer into the underlying semiconductor layer resulted in improvement in electrical performance of these solar cells containing the plasmonic Ag nano particles.

**Keywords:** Surface Plasmon Resonance, Solar cell, Thin Films, Nano particles, Flexible substrate.

## 1. INTRODUCTION

There is great interest in thin-film solar cells that can be deposited on cheap substrates such as glass, plastic or stainless steel. A limitation in all thin-film solar-cell technologies is that the absorbance of near-bandgap light is small. Therefore, structuring the thin-film solar cell so that light is trapped in the bulk so as to increase the absorbance is a subject of intense research. A significant reduction in thin-film solar-cell thickness would also allow the large-scale use of scarce semiconductor materials such as In and Te that are available in the Earth's crust. Solar-cell design and materials-synthesis considerations are strongly dictated by the requirements for optical absorption thickness- to allow near-complete light absorption and minority carrier diffusion lengths which should be several times the material thickness for all photo-carriers to be collected. In the past few years, the field of plasmonics has emerged as a rapidly expanding new area for materials and device research.

Studies illustrating the coupling of plasmons to optical emitters<sup>1</sup>; plasmon focusing<sup>2</sup>; hybridized plasmonic modes in nanoscale metal shells; nanoscale waveguiding; nanoscale optical antennas; plasmonic integrated circuits; nanoscale switches; plasmonic lasers; surface- plasmon-enhanced light-emitting diodes; imaging below the diffraction limit; and materials with negative refractive index have been reported [1-12]. The enhanced in-coupling of light into semiconductor thin films by scattering from plasmonic

nanoparticles was first recognized by Stuart and Hall, who used dense nanoparticle arrays as resonant scatterers to couple light into Si-on-insulator photo detector structures [13-15]. Metallic nanoparticles can be used as sub-wavelength scattering elements to couple and trap freely propagating plane waves from the Sun into an absorbing semiconductor thin film, by folding the light into a thin absorber layer. Scattered light acquire an angular spread in the dielectric that effectively increases the optical path length [16]. The surface plasmon resonance property of the Ag nanoparticles is highly related to the nanoparticle size and shape, local dielectric environment, and nanoparticle arrangement [17-19]. Thermal evaporation and electro-deposition are two common methods for depositing metal nanoparticles upon ITO substrates for solar cell application [20, 21]. These methods lead to poor control over the nanoparticle size, shape and inter-particle packing, which may result in loose of the near-field coupling effect existing among close-packed nanoparticles [22].

Diindium trisulfide ( $\beta\text{-In}_2\text{S}_3$ ) is a defect semiconductor that acts as a buffer layer in thin-film solar cells [23, 24].  $\beta\text{-In}_2\text{S}_3$  thin films prepared by chemical spray pyrolysis technique have a band gap of ~2.6 eV which allows them be used as good window layer material. We have earlier reported on the effect of sub-band gap illumination on the photoconductivity shown by  $\text{In}_2\text{S}_3$  [25]. We have also reported on the photoluminescence property of  $\text{In}_2\text{S}_3$  [26]. These results encouraged the possibility of constructing a solar cell which could exploit the plasmon resonance exhibited by the Ag thin film layer stacked above the window layer. Two fold actions from the layer were anticipated,

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one as a down converter and other as a passivation of the underlying defect semiconductor.

The authors have successfully deposited thin film solar cells on easily available, economic and flexible copper substrates using injection chemical vapor deposition technique (ICVD) [27]. Low temperature ICVD, may be a rational alternative to build up nanoparticle films with precisely-controlled nanoparticle density and inter-particle distance. In the present work we report on the study of coating a thin film with Ag nanostructures that support surface plasmons, on to the  $\text{Cu}_2\text{O}/\text{In}_2\text{S}_3$  heterostructure. The purpose of the study was to use Ag nano-particles thin film as an agent that could improve the photovoltaic response from the hetero-structure.

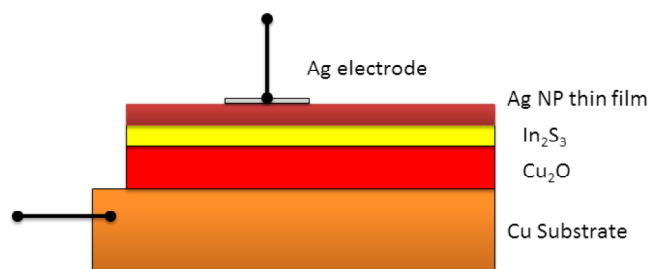
## 2. MATERIALS AND METHODS

A well-cleaned 30  $\mu\text{m}$  thick copper plate (2 cm $\times$ 1 cm) (99.0% purity) was cleaned chemically in a 2%  $\text{HNO}_3$  solution. This served as the substrate for the solar cell. In atmospheric air conditions the copper plate was then subjected to a 1 hour long annealing at 1050  $^\circ\text{C}$  in a box furnace. The substrate was then allowed to cool to 500  $^\circ\text{C}$  within the box furnace at a ramp rate of 1 $^\circ\text{C}/\text{min}$ , and then rapidly quenched to room temperature by dipping the substrate into doubly de-ionized water. One end of the substrate was then immersed in 5%  $\text{HNO}_3$  solution to remove the  $\text{Cu}_2\text{O}$  layer. This edge of width 0.5 cm was to be used for back contacting purpose. The thickness of the  $\text{Cu}_2\text{O}$  layer was found to be 980 nm using a stylus probe. The conduction type was identified to be p-type using hot probe technique.

$\text{In}_2\text{S}_3$  was deposited on to the  $\text{Cu}/\text{Cu}_2\text{O}$  structure using injection chemical vapor deposition (ICVD) technique. The details of the deposition technique have been reported earlier by us [27]. The system consists of a two zone furnace, a substrate holder and an atomizer. An airbrush with 0.25 mm nozzle serves as the atomizer which is connected to a compressor capable of delivering maximum pressure of 300 psi. The airbrush contains a gravity fed tank to store the precursor solution. In the present work we have maintained the air pressure at 60 psi during the deposition process. The temperature of zone 1 and zone 2 were maintained at 350  $^\circ\text{C}$  and 200  $^\circ\text{C}$  respectively. Precursor solution of 25 ml containing a mixture of 1.2M Indium chloride and 8M Thiourea was atomized to obtain a  $\sim$ 300 nm thick layer of  $\text{In}_2\text{S}_3$  on to the  $\text{Cu}_2\text{O}$  layer. The thickness was measured using

optical fringe technique. The conduction type was identified to be n-type using hot probe technique.

Ag nanostructures were prepared by the reduction of  $\text{Ag}^+$  solution using cane sugar juice. The reducing sugars and phenolics present in the juice are primarily responsible for the reduction of  $\text{Ag}^+$  ions to  $\text{Ag}(0)$  and its subsequent capping. To an aqueous solution of  $\text{AgNO}_3$  (2ml, 0.1M) clarified cane sugar juice was added under vigorous stirring. A reddish sol started forming after 30 min. The stirring was continued for another 30 min and the obtained colloidal solution was left in the dark for 24 hours aimed at completion of the reaction. The particles were then centrifuged (14000 rpm, 10min) and purified by four cycles of repeated centrifugation and re-dispersion in double distilled water by sonication. The solution so prepared was used to deposit a thin film using ICVD technique as described above on to the  $\text{Cu}/\text{Cu}_2\text{O}/\text{In}_2\text{S}_3$  hetero-structure. The thickness of the Ag thin films deposited was  $\sim$  80nm. The thickness was measured using optical fringe technique. A Ag electrode of 5  $\text{mm}^2$  area was deposited on to this plasmonic layer. A schematic of the cell structure is given in Figure 1. The effective area of the illuminated solar cell was 0.78  $\text{cm}^2$ .

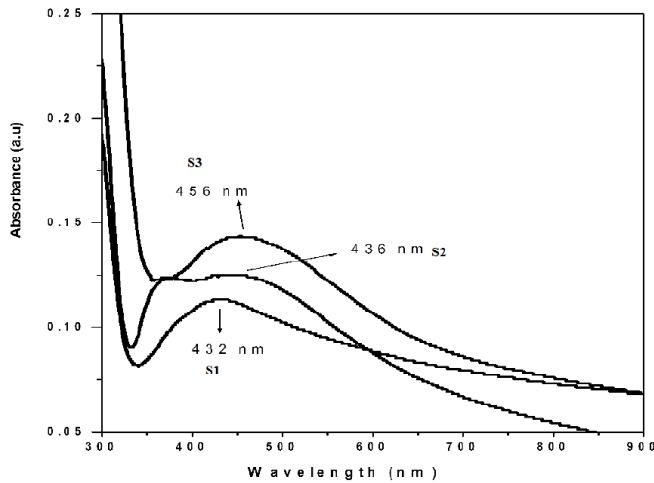


**Figure 1:** Schematic of the solar cell.

## 3. RESULTS AND DISCUSSION

The surface resistivity of  $\text{Cu}$ ,  $\text{Cu}/\text{Cu}_2\text{O}$ ,  $\text{Cu}/\text{Cu}_2\text{O}/\text{In}_2\text{S}_3$  and  $\text{Cu}/\text{Cu}_2\text{O}/\text{In}_2\text{S}_3/\text{Ag@NP}$  were measured by four probe technique. They were found to be  $10^{-2}$ , 1363, 10657 and 945  $\Omega/\text{cm}$  respectively. Figure 2 shows the surface plasmon resonance peak observed for the thin film with Ag nano-particles. The plasmon resonance peak was observed between 432 nm (2.875 eV) to 456 nm (2.72 eV), depending upon the temperature profile used for the zones. For the Ag film prepared with zone 1 at 150  $^\circ\text{C}$  and zone 2 at 200  $^\circ\text{C}$  the plasmon resonance peak was located at 432 nm. These films are hereafter named S1. When the film was deposited with zone 1 at 150  $^\circ\text{C}$  and zone 2 at 150  $^\circ\text{C}$  the resonance peak was observed at 436 nm.

These films are named as S2 in this report. For films grown with zone 1 at 150 °C and zone 2 at 100 °C the resonance peak was observed at 456 nm. These films are named S3 hereafter Ag films could not be deposited with zone 2 at temperatures above 220 °C. This could be because of oxidation of Ag at higher temperatures.



**Figure 2:** Plasmon resonance for the thin films with Ag nanostructures.

The plasmon resonance peak can be assigned to Surface Plasmon Resonance (SPR) of silver nanoparticles. Plasmon resonance of nanoparticles can be explained within the Mie theory. According to the Mie theory, the surface resonance can be described by the following equation. [24]

$$\omega_r = \frac{\omega_p}{\sqrt{\epsilon_m + \epsilon_l}} \quad (1)$$

where,

$\omega_p$  is the bulk plasmon resonance which is about 9 eV for Ag [28]

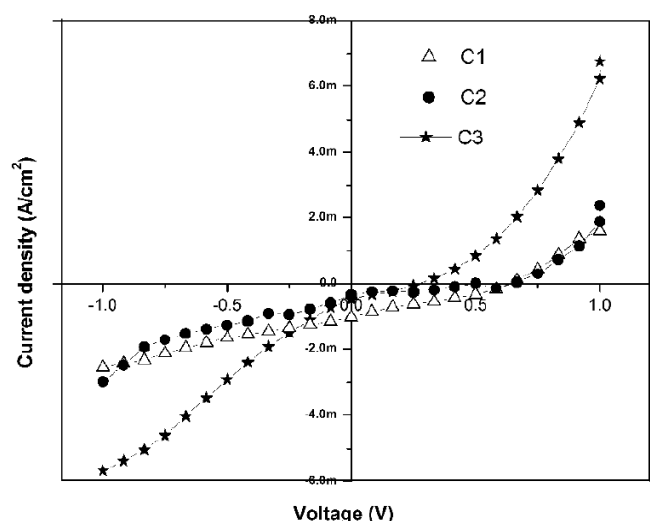
$\epsilon_m$  : Dielectric constant for the matrix = 1 for vacuum.

$\epsilon_l$  : Dielectric constant for Ag which is ~5. [29]

Based on relation (1) the surface plasmon resonance of Ag is calculated to be 3.67eV. When Ag particles are embedded in certain matrix, its work function will decrease compared to that in vacuum, which will lower the energetic position of the surface resonance state. So the energetic position of surface resonance state of Ag particle in vacuum is higher than that of Ag particle embedded in any other matrix. The work function of Ag particles embedded in different

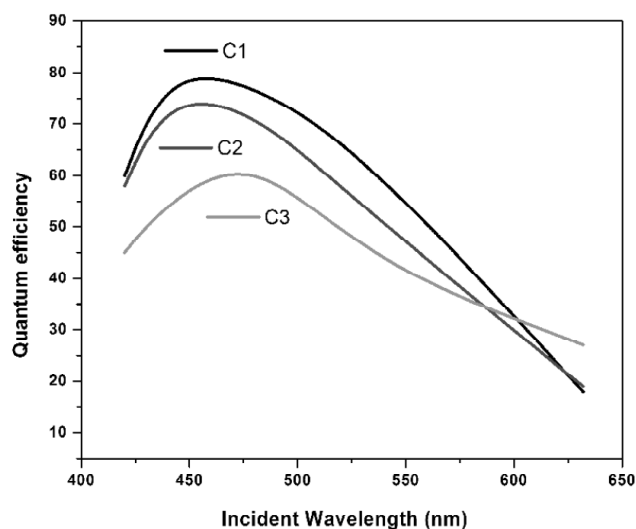
matrix is different, which will reduce the energetic position of surface resonance state to different degrees. Thus we may explain the lowering of the SPR on the basis of the organic matrix in which Ag is embedded in our thin films. The inset in Figure 2 shows the Plasmon resonance observed for the solution used for thin film growth. The resonance peak is observed at 449 nm. The SPR absorption spectra for Ag NP solid thin film, showed both blue and red shift compared to NPs in solution. There is a blue shift in the resonance peak when thin films are deposited using the solution with zone 2 maintained at temperatures above zone 1. Red shift was observed for Ag thin films when zone 2 was maintained at temperatures below zone 1. The shift observed is in accordance to the inter-particle coupling effect. When deposition occurs with zone 2 at lower temperature than zone 1 the reduced thermal agitation on the substrate surface may be leading to the observed red shift in SPR of the deposited thin films.

Individual solar cells were fabricated using S1, S2 and S3. These cells are named as C1, C2 and C3 to indicate that they contain the nano-Ag film S1, S2 and S3 respectively. Figure 3 shows the current-voltage characteristics of these solar cells. The inset in Figure 3 shows the dark I-V characteristics, which exhibits non-ideal diode behavior. There are in general three aspects of non-ideal diode behavior in a p-n junction: (1) the amount of recombination as a function of bias, (2) the breakdown behavior, and (3) the nature of ohmic shunts. The current contribution in the dark is caused by recombination in the depletion region which contributes significantly to the diode's total external current. The illuminated current-voltage characteristics were recorded for these solar cells under white light illumination of 100 mW/cm<sup>2</sup>. The electrical performances of these cells are improved compared to the previously reported results for the Cu<sub>2</sub>O/In<sub>2</sub>S<sub>3</sub> hetero-structure. [27] The open circuit voltage of the best cell (C1) is 0.65 V, with short circuit current density of 1.2 mA/cm<sup>2</sup>, fill factor of 22% and efficiency 0.17%. The previously reported electrical parameters for this hetero-structure were  $V_{oc} = 0.377$  V and  $J_{sc} = 0.118$  mA/cm<sup>2</sup>. [27] The short circuit current exhibited a linear dependence on illumination intensity whereas the open circuit voltage resembled Arrhenius dependence for the solar cell. Based on the illumination intensity dependence of open circuit voltage and short circuit current we could conclude that the junction was symmetric in nature.



**Figure 3:** Illuminated current voltage characteristic of the three solar cells.

Figure 4 shows the results of the relative quantum efficiency (QE) measurement carried out for the solar cells. The relative efficiency is low for the long wavelength region and improves for the shorter wavelength region. From the figure it is observed that the maximum quantum efficiency for cell C1 is measured for  $\sim 2.74$  eV. For cells C2 and C3 the peak QE is shifted towards the red region compared to the cell C1. In general there is a significant shift to the blue wavelength region for the cells as compared to the quantum efficiency measurements reported for the  $\text{Cu}_2\text{O}/\text{In}_2\text{S}_3$  solar cell without the plasmonic layer [27]. The shift can be explained in terms of the strong local field enhancement around the Ag nanoparticles. In our solar cell the strong local field enhancement around the Ag nanoparticles embedded in the organic matrix may



**Figure 4:** Quantum efficiency measured for the three solar cells.

be increasing the absorption in the semiconductor material. This is supported by the observed increase in short circuit current density for the cell. This is also supported by the observation that cell C1 has larger short circuit current compared to the other cells.

#### 4. CONCLUSIONS

We have been able to grow thin films with Ag nanoparticles confined in an organic matrix using injection chemical vapor deposition technique. The plasmon resonance in the film was blue shifted compared to the plasmon resonance in the precursor solution for the Ag nanoparticles. These thin films when coated over the  $\text{Cu}_2\text{O}/\text{In}_2\text{S}_3$  solar cell resulted in enhanced electrical performance. The current density in these solar cells having the plasmonic layer increased as compared to their counterparts where the plasmonic layer was absent. We conclude that plasmonic near-field in the Ag nanoparticles thin film was coupled to the hetero-junction, which increased the effective absorption cross-section for the blue region of the spectrum in the buffer layer and in the solar cell. This was supported by the observed shift to blue region and increase in quantum efficiency for the solar cell compared to their counterparts. Thus we have been able to demonstrate improvement in photovoltaic effect in the  $\text{Cu}_2\text{O}/\text{In}_2\text{S}_3$  solar cell using silver nanoparticles.

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#### REFERENCE

- [1] Kühn S, Hakanson U, Rogobete L, Sandoghdar V. 2006, *Phys. Rev. Lett.* 97, 017402. <http://dx.doi.org/10.1103/PhysRevLett.97.017402>
- [2] Verhagen E, Spasenović M, Polman A, Kuipers L. 2008, *Phys. Rev. Lett.* 102, 203904. <http://dx.doi.org/10.1103/PhysRevLett.102.203904>
- [3] Prodan E, Radloff C, Halas NJ, Nordlander P. 2003, *Science*, 302, 419. <http://dx.doi.org/10.1126/science.1089171>
- [4] Zia R, Selker MD, Catrysse PB, Brongersma ML. 2004, *J. Opt. Soc. Am. A* 21, 2442. <http://dx.doi.org/10.1364/JOSAA.21.002442>
- [5] Mühlischlegel P, Eisler HJ, Martin OJF, Hecht B, Pohl DW. 2005, *Science* 308, 1607. <http://dx.doi.org/10.1126/science.1111886>
- [6] Bozhevolnyi SI, Volkov VS, Devaux E, Laluet JY, Ebbesen. 2006, *T.W. Nature*, 440, 508. <http://dx.doi.org/10.1038/nature04594>

- [7] Krasavin AV, Zheludev NI. 2004, Appl. Phys. Lett. 84, 1416. <http://dx.doi.org/10.1063/1.1650904>
- [8] Oulton RF. 2009, Nature 461, 629. <http://dx.doi.org/10.1038/nature08364>
- [9] Okamoto K. 2004, Nature Mater. 3, 601. <http://dx.doi.org/10.1038/nmat1198>
- [10] Pendry JB. 2000, Phys. Rev. Lett. 85, 3966. <http://dx.doi.org/10.1103/PhysRevLett.85.3966>
- [11] Shelby RA., Smith DR, Schultz S. 2001, Science 292, 77. <http://dx.doi.org/10.1126/science.1058847>
- [12] Linden S. 2004, Science 306, 1351. <http://dx.doi.org/10.1126/science.1105371>
- [13] Stuart HR, Hall DG. 1996, Appl Phys Lett 69, 2327. <http://dx.doi.org/10.1063/1.117513>
- [14] Stuart HR, Hall DG. 1998, Appl Phys Lett 73, 3815. <http://dx.doi.org/10.1063/1.122903>
- [15] Harry A. Atwater, Albert Polman. 2010, Nature Materials, 9,205. <http://dx.doi.org/10.1038/nmat2629>
- [16] Kelly KL, Coronado E, Zhao LL, Schatz GC. 2002, Journal of Physical Chemistry B 107,668. <http://dx.doi.org/10.1021/jp026731y>
- [17] Cheng YN, Wang M, Borghs G, Chen HZ. 2011, Langmuir 27,7884. <http://dx.doi.org/10.1021/la200840m>
- [18] Yang Y, Matsubara S, Nogami M, Shi JL. 2007, Materials Science and Engineering B 140, 172. <http://dx.doi.org/10.1016/j.mseb.2007.03.021>
- [19] Morfa AJ, Rowlen KL, Reilly TH, Romero MJ, Lagemaat JVD. 2008, Applied Physics Letters 92, 013504. <http://dx.doi.org/10.1063/1.2823578>
- [20] Kim SS, Na SI, Jo J, Kim DY, Nah YC. 2008, Applied Physics Letters 92, 073307. <http://dx.doi.org/10.1063/1.2967471>
- [21] Yoon WJ, Jung KY, Liu J, Duraisamy T, Revur R, Teixeira, S. Sengupta, P.R. Berger, 2010, Solar Energy Materials FL, Solar Cells 94,128. <http://dx.doi.org/10.1016/j.solmat.2009.08.006>
- [22] Rocca M. 1995, Surf. Sci. Rep., 22, 1. [http://dx.doi.org/10.1016/0167-5729\(95\)00004-6](http://dx.doi.org/10.1016/0167-5729(95)00004-6)
- [23] Teny Theresa John, Sudha Kartha C, Vijayakumar KP, Abe T, Kashiwaba Y. 2005, Sol. Energy Mater. Sol. Cells 89, 27 <http://dx.doi.org/10.1016/j.solmat.2004.12.005>
- [24] Jayakrishnan R, Teny Theresa John Sudha Kartha C, Vijayakumar KP, Deepthi Jain, Sarath Chandran, Ganeshan V. 2008, J Appl Phys 103, 053106 <http://dx.doi.org/10.1063/1.2841488>
- [25] Jayakrishnan R, Tina Sebastian, Teny Theresa John, C.Sudha Kartha Vijayakumar KP. 2007, J Appl Phys 102, 043109 <http://dx.doi.org/10.1063/1.2770830>
- [26] Jayakrishnan R, Teny Theresa John, Sudha Kartha CVijayakumar KP, Abe T, Kashiwaba Y. 2005, Semi. Cond. Sci. and Tech. 20, 1162 <http://dx.doi.org/10.1088/0268-1242/20/12/003>
- [27] Jayakrishnan R. 2013, Materials Science in Semiconductor Processing, 16 (6), 1608. <http://dx.doi.org/10.1016/j.mssp.2013.04.018>
- [28] Ehrenreich E, Philipp H. 1962, Phys. Rev., 128, 1622. <http://dx.doi.org/10.1103/PhysRev.128.1622>
- [29] Chen CF, Tzeng SD, Chen HY, Lin KJ, Gwo S. 2008, Journal of the American Chemical Society 130, 824. <http://dx.doi.org/10.1021/ja0773610>

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