

“Optical properties of thin films with plasmonic effect for light scattering”, K. Lovchinov, O. Angelov, D. Dimova-Malinovska, (2012) J. Phys. in press

# Optical properties of thin films with plasmonic effect for light scattering

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**Abstract.** Thin films of Al<sub>2</sub>O<sub>3</sub> with embedded Cu and Ag nanoparticles (NPs) are deposited by r.f. co-sputtering on glass substrates. The samples are annealed at 400<sup>0</sup>C and 500<sup>0</sup>C for 3 h in forming gas (N<sub>2</sub>+5% H<sub>2</sub>) to stimulate Cu and Ag nanoclusters' formation. Multilayer structures (stacks) such as Al<sub>2</sub>O<sub>3</sub>/Ag/Al<sub>2</sub>O<sub>3</sub>, ZnO:Al/Ag/ZnO:Al and Ag/ZnO:Al/Ag/ZnO:Al are deposited on glass substrate by consequently sputtering of the individual layers. Before deposition of the capping layers of Al<sub>2</sub>O<sub>3</sub> and ZnO:Al, the bi-layer structures are annealed in vacuum for 50 min at 220<sup>0</sup>C or 400<sup>0</sup>C in the case of glass/Al<sub>2</sub>O<sub>3</sub>/Ag, and at 220<sup>0</sup>C in the case of glass/ ZnO:Al/Ag and glass/ Ag/ZnO:Al/Ag. The diffuse and specular reflectance and transmittance spectra are measured in the spectral range of 300-1200 nm to study the plasma resonance of Cu and Ag nanoparticles. The optical properties of the films and the stack structures are discussed.

## 1. Introduction

One of the main goals of the researchers' community involved in solar cells technology nowadays is decreasing of the cost of the solar cells together with increasing of their efficiency [1]. In parallel with the advance of research in nanotechnology, many researchers are now utilising nanophotonics in order to increase the efficiency of thin film solar cells [2]. Surface plasmon (SP) resonance can be employed to enhance light absorption in thin film solar cells, thanks to the scattering caused by noble metal nanoparticles or islands deposited on the semiconductor surface.

One topic that attracts a lot of attention is the use of metallic nanoparticles (NPs) at the front or at the rear side of thin film solar cells [3,4]. The introduction of noble metal nanoparticles into or on solar cells is able to induce a significant increase of the photocurrent since two main phenomena can take place nearby those objects: light scattering and near-field concentration of light. This can be realized by deposition of metal nanoparticles on the top surface of the solar cell and back reflector with metal nanoparticles at the bottom of the solar cell to direct the unabsorbed incident light to the adjacent junction [5, 6]. The absorption in the solar cell thus can be improved for an individual part of the spectrum or for a wide wavelengths range. This requires development of different thin films and multilayer structures with appropriate optical properties based on embedded metal nanoparticles with optimal size, shape and distribution to establish advantages other than those achievable with the

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standard light trapping methods [7]. Recently plasmon structures for light-trapping concept on localizes surface plasmon polariton induced light scattering at nanostructures Ag back contacts of thin-film silicon solar cells has been proposed, designed and theoretically simulated [4].

In this article the results of study of the optical properties of thin films of  $\text{Al}_2\text{O}_3$  with embedded Cu and Ag nanoparticles and of multilayer stacks, namely  $\text{Al}_2\text{O}_3(13\text{nm})/\text{Ag}(10\text{nm})/\text{Al}_2\text{O}_3(47\text{nm})$ ,  $\text{ZnO:Al}(90\text{nm})/\text{Ag}(10\text{nm})/\text{ZnO:Al}(43\text{nm})$  and  $\text{Ag}(100\text{nm})/\text{ZnO:Al}(180\text{nm})/\text{Ag}(10\text{nm})/\text{ZnO:Al}(43\text{nm})$  deposited by r.f. magnetron co-sputtering and sputtering on glass substrates are reported. The numbers in the bracket indicate the thickness of the corresponding films. The co-sputtered films with embedded Cu and Ag nanoparticles and the intermediate structures  $\text{glass}/\text{Al}_2\text{O}_3(13\text{nm})/\text{Ag}(10\text{nm})$  and  $\text{glass}/\text{ZnO:Al}(90\text{nm})/\text{Ag}(10\text{nm})$  (before deposition of the  $\text{Al}_2\text{O}_3$  and ZnO:Al capping layer) are thermally treated at different temperatures and atmospheres to stimulate the formation of Cu and Ag nanoparticles with plasma resonance properties.

## 2. Experimental

The method of r.f. magnetron sputtering (13.56 MHz) is used to deposit the studied films and multilayer structures. The substrates are glass plates ultrasonically cleaned before deposition.  $\text{Al}_2\text{O}_3$  films with embedded Cu and Ag are deposited by co-sputtering of  $\text{Al}_2\text{O}_3$  ceramic target with both Cu and Ag plates in the zone of maximum erosion in atmosphere of Ar (0.5 Pa). The applied r.f power is 160 W. Two different sets of samples of  $\text{Al}_2\text{O}_3$  with embedded Cu and Ag are deposited, where the area of Cu ( $S_{\text{Cu}}$ ) and Ag ( $S_{\text{Ag}}$ ) plates are different: set 1 -  $S_{\text{Cu}} = 45 \text{ mm}^2$  and  $S_{\text{Ag}} = 15 \text{ mm}^2$ , and set 2 -  $S_{\text{Cu}} = 55 \text{ mm}^2$  and  $S_{\text{Ag}} = 20 \text{ mm}^2$ . The substrates have not been deliberately heated during the deposition. The thickness of the deposited films is about 70 nm. The obtained films of  $\text{Al}_2\text{O}_3$  with embedded Cu and Ag are annealed in forming gas -  $\text{N}_2 + (5\%) \text{ H}_2$ , for 3h at  $400^\circ\text{C}$  or  $500^\circ\text{C}$ . The multilayer structures  $\text{glass}/\text{Al}_2\text{O}_3(13\text{nm})/\text{Ag}(10 \text{ nm})/\text{Al}_2\text{O}_3(47 \text{ nm})$  are deposited in sequence by sputtering of  $\text{Al}_2\text{O}_3$  ceramic target, Ag target and  $\text{Al}_2\text{O}_3$  ceramic target on glass substrate without heating.

The ZnO:Al films in the multilayer structures  $\text{glass}/\text{ZnO:Al}(90\text{nm})/\text{Ag}(10 \text{ nm})/\text{ZnO:Al}(43 \text{ nm})$  are obtained by sputtering of target ( $\text{ZnO} + (2 \text{ wt.}\%) \text{ Al}$ ) and the Ag film of Ag target. The ZnO:Al films are deposited at substrate temperature,  $T_s$ , of  $100^\circ\text{C}$ , and the Ag film without heating of the substrate. The r.f. power is 160 W in the case of deposition of oxide films ( $\text{Al}_2\text{O}_3$  and ZnO:Al) and 65 W in the case of Ag films. The thickness of the films in the multilayer structures is indicated in the brackets. Before deposition of the capping layers of  $\text{Al}_2\text{O}_3$  and ZnO:Al, the bi-layer structures are annealed in vacuum 50 min at  $220^\circ\text{C}$  and  $400^\circ\text{C}$  in the case of  $\text{glass}/\text{Al}_2\text{O}_3/\text{Ag}$ , and at  $220^\circ\text{C}$  in the case of  $\text{glass}/\text{ZnO:Al}/\text{Ag}$  or  $\text{glass}/\text{Ag}/\text{ZnO:Al}/\text{Ag}$ .

The spectra of transmittance and reflectance are measured in the range of 300-1200 nm to study the optical properties of the thin films and the multilayer structures before and after thermal treatment. The spectra of the individual layers after deposition and annealing at different stage of preparation of the multilayer structures are presented as well. The haze ratio in transmission and in reflection for the multilayer structures are calculated using the spectra of specular and diffuse transmittance or reflectance, respectively, which demonstrate the light scattering from the metal nanoparticles. The reflectance and transmittance spectra of the films are measured by Shimadzu 3100 spectrophotometer. The films thickness is measured by profilometer "Talystep" with accuracy of 3%.

## 3. Results and discussion.

The technological conditions of deposition of the obtained layers and multilayer structures are presented in Table 1. The data obtained from the optical characterization of the films and the structures (the peak positions of the band due to the plasma resonance in the transmittance and reflectance spectra) are given in Table 2 and Table 3, respectively.

Figures 1a and 1b show the transmittance and the reflectance spectra, respectively, of thin films  $\text{Al}_2\text{O}_3$  with embedded Cu and Ag nanoparticles for both sets of samples.

**Table 1.** Technological condition of deposition of the thin films and multilayer structures. The thickness and the substrate temperature,  $T_s$ , of the individual layers in the multilayer structures are given in a sequence of the deposition.

Sample	Thickness, [nm]	$T_s$ , [ $^{\circ}$ C]	Annealing
Glass/ $Al_2O_3$ :Cu:Ag – set 1 $S_{Cu}=45mm^2$ ; $S_{Ag}=15mm^2$	70	without heating	400 $^{\circ}$ C, 3h, $N_2+H_2$ or 500 $^{\circ}$ C, 3h, $N_2+H_2$
Glass/ $Al_2O_3$ :Cu:Ag – set 2 $S_{Cu}=55mm^2$ ; $S_{Ag}=20mm^2$	70	without heating	400 $^{\circ}$ C, 3h, $N_2+H_2$ or 500 $^{\circ}$ C, 3h, $N_2+H_2$
Glass/ $Al_2O_3$ /Ag/ $Al_2O_3$	13/10/47	all layers without heating	Ag(10 nm)- vacuum, 50 min., 220 $^{\circ}$ C or 400 $^{\circ}$ C
Glass/Ag/ZnO:Al/Ag/ZnO:Al	100/180/10/43	without heating/100 $^{\circ}$ C/without heating/100 $^{\circ}$ C	Ag(10 nm)-vacuum, 50 min., 220 $^{\circ}$ C
Glass/ZnO:Al/Ag/ZnO:Al	90/10/43	100 $^{\circ}$ C/without heating/100 $^{\circ}$ C	Ag(10 nm)- vacuum, 50 min., 220 $^{\circ}$ C

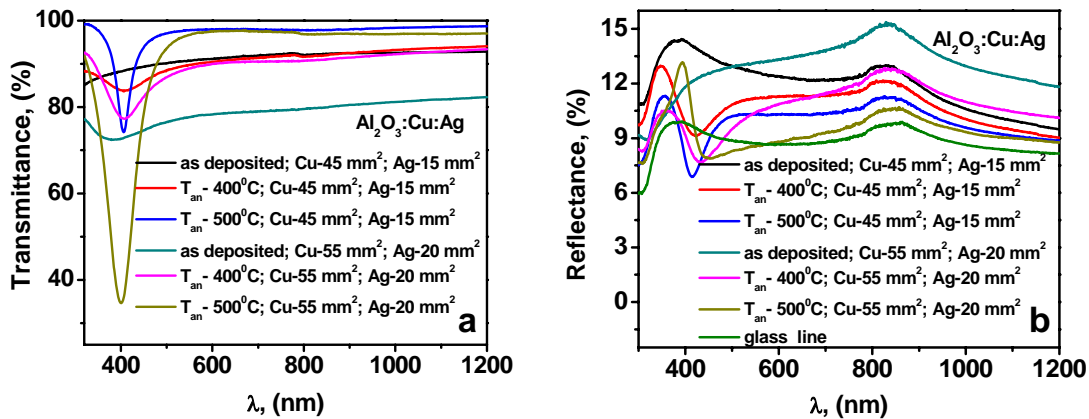
**Table 2.** Positions of the plasma resonance bands in the transmittance spectra.

Sample	as deposited	$T_{an.}$ , 220 $^{\circ}$ C	$T_{an.}$ , 400 $^{\circ}$ C	$T_{ann.}$ , 500 $^{\circ}$ C	After capping (Ag-220 $^{\circ}$ C)	After capping (Ag-400 $^{\circ}$ C)
$Al_2O_3$ :Cu:Ag - set 1 $S_{Cu}=45mm^2$ ; $S_{Ag}=15mm^2$	-	-	406 nm	405 nm	-	-
$Al_2O_3$ :Cu:Ag - set 2 $S_{Cu}=55mm^2$ ; $S_{Ag}=20mm^2$	387 nm	-	406 nm	400 nm	-	-
$Al_2O_3$ /Ag/ $Al_2O_3$	493 nm	469 nm	432 nm	-	472 nm	457 nm
Ag/ZnO:Al/Ag/ZnO:Al						
ZnO:Al/Ag/ZnO:Al	502 nm	512 nm	-	-	-	-

**Table 3.** Positions of the plasma resonance bands in the reflectance spectra.

Sample	as deposited	$T_{an.}$ , 220 $^{\circ}$ C	$T_{an.}$ , 400 $^{\circ}$ C	$T_{ann.}$ , 500 $^{\circ}$ C	After capping (Ag-220 $^{\circ}$ C)	After capping (Ag-400 $^{\circ}$ C)
$Al_2O_3$ :Cu:Ag – set 1 $S_{Cu}=45mm^2$ ; $S_{Ag}=15mm^2$	-	-	420 nm	415 nm	-	-
$Al_2O_3$ :Cu:Ag – set 2 $S_{Cu}=55mm^2$ ; $S_{Ag}=20mm^2$	-	-	432 nm	450 nm	-	-
$Al_2O_3$ /Ag/ $Al_2O_3$	496 nm	476 nm	433 nm	-	497 nm	469 nm
Ag/ZnO:Al/Ag/ZnO:Al		430 nm				
ZnO:Al/Ag/ZnO:Al	495 nm	518 nm	-	-	459 nm	-

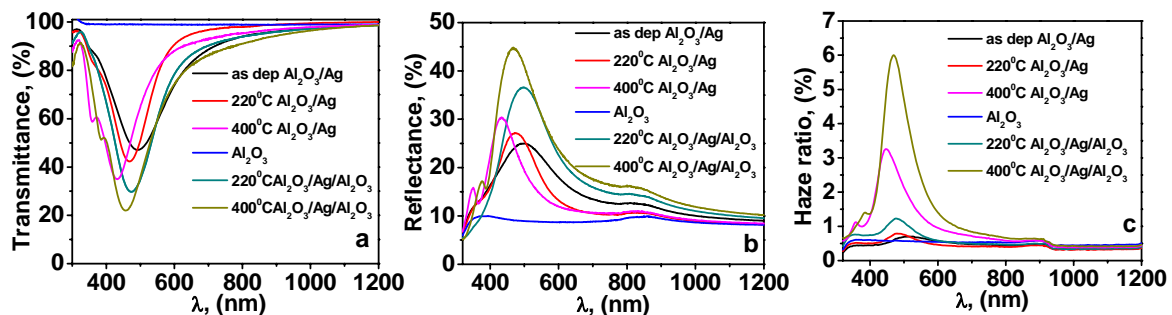
In the transmittance spectra of the as-deposited films the plasma resonance due to the Ag nanoparticles at about 400 nm is observed only in the set -2 (with higher area of Cu and Ag plates). The transmittance spectra of the films with embedded Cu and Ag NPs (figure 1a) for the both sets of samples after annealing demonstrate band of absorption at about 400 nm due to the plasma resonance of Ag nanoparticles more pronounced for the set 2 and after annealing at higher temperature - 500°C. A smeared plasma resonance band due to the Cu in the spectral range of 600-800 nm could be scarcely seen only after high increasing of the scale performance.



**Figure 1.** Transmittance (a) and reflectance (b) spectra of  $\text{Al}_2\text{O}_3$  with embedded Cu and Ag for set 1 and set 2.

The reflectance spectra of the as-deposited films (figure 1b) for the both sets of samples demonstrate the absence of plasma resonance. The comparison with the spectrum of reflectance of the bare glass substrate in the same figure (figure 1b) confirms this. The band near 850 nm in the reflectance spectra is an artefact due to change of the detectors in the spectrophotometer. After annealing the band due to the plasma resonance of Ag NPs appears in the spectra of reflection at about 400 nm.

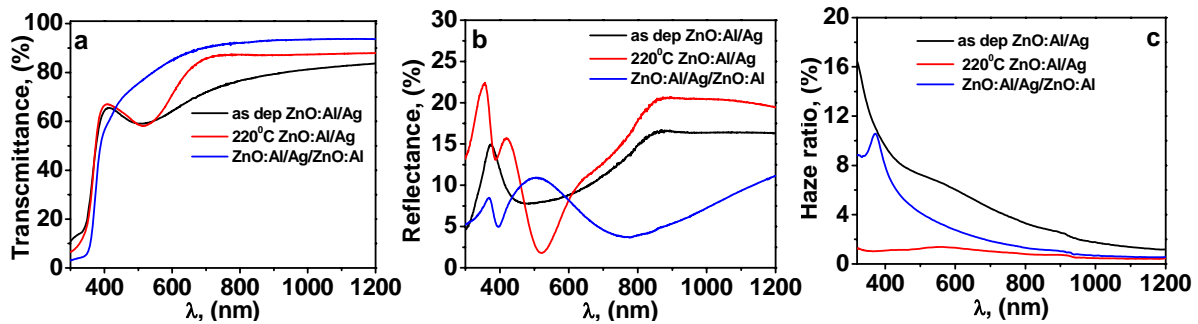
It is obvious that the higher annealing temperature provides better conditions for diffusion of metal nanoparticles and formation of larger NPs in the dielectric film. The formation of bigger metal nanoparticles with better size distribution results in more narrow plasma resonance band with higher intensity [8]. The observed plasma resonance in the samples based on dielectric  $\text{Al}_2\text{O}_3$  thin film with embedded metal NPs demonstrate the possibility for their application in solar cell structures to enhance the light absorption.



**Figure 2.** Transmittance (a) and reflectance (b) spectra and haze ratio in transmission (c) of the deposited films and structures at different stages of their preparation of the steak glass/ $\text{Al}_2\text{O}_3$ (13 nm)/Ag(10 nm)/ $\text{Al}_2\text{O}_3$ (47 nm) - as deposited and annealed in vacuum at 220°C and 400°C 50 min.

The spectra of transmittance, reflectance and the haze ratio in transmittance of multilayer structure glass/Al<sub>2</sub>O<sub>3</sub>(13nm)/Ag(10 nm)/Al<sub>2</sub>O<sub>3</sub>(47 nm), are presented in figures 2a, 2b and 2c, respectively. The corresponding spectra on different stage of preparation of the multilayer structures are shown, as well. The spectra of pure Al<sub>2</sub>O<sub>3</sub> thin film are given for comparison, as well.

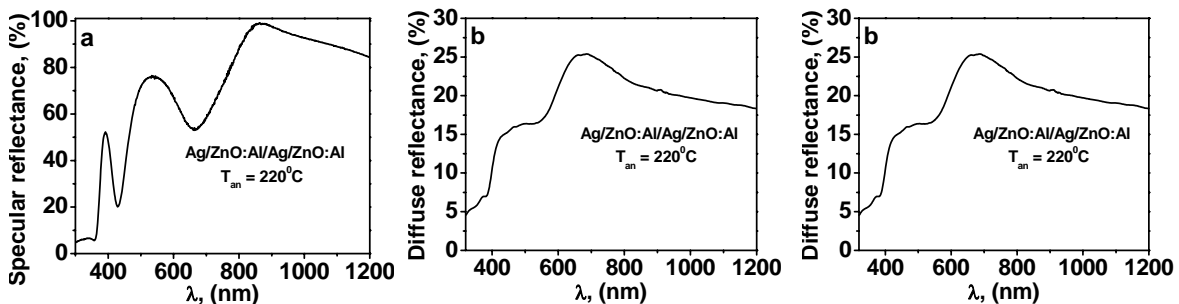
The transmittance and reflectance spectra (figures 2a and 2b) after deposition of Ag (10 nm) layer in the stack glass/Al<sub>2</sub>O<sub>3</sub>(13 nm)/Ag(10 nm)) show broad band of absorption at about 493 nm due to the plasma resonance of Ag NPs. After annealing the plasma resonance band position shifts to the lower wavelengths (at T<sub>ann</sub> = 400<sup>0</sup>C it is observed at 432 nm) and its intensity increases. The shift of the plasmon band to the higher wave length higher than 400 nm indicates the presence of nanoparticles with shape different from the spherical [9].



**Figure 3.** Transmittance (a) and reflectance (b) spectra and haze ratio in transmission (c) of thin films ZnO:Al(90 nm)/Ag(10 nm)/ZnO:Al(43 nm).

The haze ratio in transmission of glass/Al<sub>2</sub>O<sub>3</sub>(13 nm)/Ag(10nm) and glass/Al<sub>2</sub>O<sub>3</sub>(13 nm)/Ag(10 nm)/Al<sub>2</sub>O<sub>3</sub>(47 nm) multilayer structure has higher values and demonstrates higher pronounced scattering of light in the range of 400-600 nm after annealing of Ag (10 nm) layer at 400<sup>0</sup>C. In the spectra of transmission, reflectance and of haze ratio in transmission of this stack before and after deposition of the capping Al<sub>2</sub>O<sub>3</sub> layer, additional weak band of multiple plasma resonance bands at wave lengths lower than 400 nm are observed due to multiple absorption in the Ag nanoparticles [10].

The spectra of transmittance, reflectance and the haze ratio in transmission of multilayer structure glass/ZnO:Al(90 nm)/Ag(10 nm)/ZnO:Al(43 nm) are presented in figures 3a, 3b and 3c, respectively. The transmittance spectra of as-deposited and annealed structure glass/ZnO:Al(90 nm)/Ag(10 nm) demonstrate plasma resonance with broad band positioned at about 503 nm and 512 nm, respectively, more pronounced after annealing. The shift of the plasma resonance band to the higher wavelengths demonstrates that the shape of the Ag nanoparticles deviates from the spherical form and their size is different from the optimal one for Ag plasma resonance which is 200-250 nm [9]. After capping by ZnO:Al film of the annealed glass/ZnO:Al(90 nm)/Ag(10 nm) structures the band of plasma resonance in the transmission spectra smears.



**Figure 4.** Specular reflectance (a) diffuse reflectance (b) spectra and haze ratio in reflection of multilayer structure Ag(100nm)/ZnO:Al(180nm)/Ag(10nm)/ZnO:Al(43 nm).

The haze ratio in transmission of the multilayer structure glass/ZnO:Al(90nm)/Ag(10 nm)/ZnO:Al(43 nm) has the highest value in the whole spectral region which demonstrate higher scattering of light. This kind of multilayer structure is deposited on glass coated with Ag reflector layer with thickness of 100 nm. The same consequence of technological processes and conditions of deposition and thermal treatment are applied. Figures 4a and 4b demonstrate the specular reflectance spectra and the diffuse reflectance spectra of the stack glass/Ag(100 nm)/ZnO:Al(90nm)/Ag(10nm)/ZnO:Al(43nm), respectively. The typical band of plasma resonance of Ag nanoparticles is observed at about 430 nm. The intensity of the band is less pronounced in the spectrum of diffuse reflectance (figure 4b). The values of reflectance of the stack deposited on the Ag reflector film are much higher in the whole spectral region under investigation than in the multilayer structures without Ag reflector. The haze ratio in reflectance (figure 4c) suggest for higher scattering of the light than in the multilayer structure without deposited Ag mirror on the glass substrate. This demonstrates that such multilayer structure deposited on Ag reflector layer can be applied on the back side of the thin film solar cells for increasing the back scattering of the unabsorbed light.

#### 4. Conclusion.

The optical properties of thin films of Al<sub>2</sub>O<sub>3</sub> with embedded Cu and Ag nanoparticles deposited by r.f. magnetron sputtering on glass are studied. The transmittance spectra of the films demonstrate absorption band of plasma resonance of Ag nanoparticles at about 400 nm more pronounced for the higher plates area of Ag and Cu and after annealing at higher temperature-500<sup>0</sup>C. A very weak smeared band of plasma resonance at about 600-900 nm due to the Cu nanoparticles can be hardly observed. The plasma resonance peak intensity in transmittance spectra increases after annealing at 500<sup>0</sup>C. The reflectance spectra of the as-deposited films demonstrate the absence of plasma resonance. After annealing the band of Ag plasma resonance in the reflectance spectra appears at about 400 nm. The haze ratio in transmission demonstrates scattering of light in a broad wavelengths range. The study of the optical properties of the multilayer structures reveal the presence of the plasma resonance band(s) in the spectra of transmission, reflection and haze ratio of transmission or reflection due to the presence of thin Ag nanostructured film. After deposition of the capping ZnO:Al layer the intensity of the plasma absorption band decreased and this need further investigation to establish the reason. The stack structure with ZnO:Al layers deposited on Ag back reflector demonstrates high values of specular and diffuse reflection. The obtained results show that such multilayer structure can be applied on the back side of the thin film solar cells for increasing the back scattering of the unabsorbed light. The observed plasma resonance in the films and the multilayer structures under investigation can be enhanced by optimal size, shape and distribution of the nanoparticles designed through new optimal technology conditions at future studies.

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