Study of LSPR-Enhanced Absorption for Solar Cell Applications: Preliminary results

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ABSTRACT

The Localized Surface Plasmon Resonance (LSPR) phenomenon exhibited in nano-particles, embedded in a dielectric medium has recently been shown to enhance the absorption as well as the photo-generation effect in several light-sensitive structures including solar cells and photo-diodes .The origin of this enhancement has not yet been sufficiently clarified as there appear to be several mechanisms at play, depending on the particular device structure and configuration. We have conducted computer simulation studies on the absorption enhancement in a silicon substrate by nano-shell-related LSPR, based on a Finite Difference, Time-Domain (FDTD) Analysis.

Preliminary results of this study show significant enhancement of up to **10X** in the near band gap spectral region of Si, using 40-100nm diameter nano-shells. The enhancement was studied as a function of the metallic Shell thickness, the thickness of an externally coating layer of SiO_2, as well as of various nanoshell shapes. The results suggest that the main enhancement mechanism in this case of tubular nanoshells embedded in Si substrate, is that of field-enhanced absorption caused by the strongly LSPR-enhanced electric field extending into the Silicon substrate.

Keywords: Solar Cell, Photovoltaic, LSPR, Nano Particle, Nano Shell, Absorption, Field Enhancement.

1. INTRODUCTION

Solar cell technology is considered one of the main approaches in satisfying the critical need for renewable, non-fossil sources of energy. The photovoltaic industry has seen extraordinary annual growth rates of over 30% in the last few years following improvements in the efficiency and the demand for alternative energy resources. One of the key photovoltaic materials is the Silicon, considered one of the best candidates for large scale photovoltaic conversion of sunlight [1]. However, the indirect bandgap of crystalline Si (c-Si) normally requires the use of thick layers of ~100 μm, in order to obtain sufficient absorption of the near infrared radiation. This in turn requires the use of pure materials with long minority carrier diffusion length, which increases costs and energy payback time. Hence, strategies for enhanced light absorption need to be explored to enable efficient light harvesting by thinner photoactive layers. One approach is to exploit the large optical cross sections associated with localized surface plasmon resonances (LSPRs) generated in metallic nano-particle to enhance the electron-hole (e-h) pair generation in the nearby Si substrate [1]**,** [**2**]. Surface plasmons, or surface Plasmon polaritons, are electron density fluctuations at the interface between a metal and a dielectric material. Such resonant modes can be excited at the surface of nanoparticles, by an incoming plane wave. These LSPR modes exhibit a marked, tunable resonance. For frequencies near the resonance, nanoparticles have an optical cross section much larger than their geometrical cross section. Furthermore, this resonance can be tuned to match the band gap of silicon or other photo-substrates as required. Such LSPR resonance can lead to a dramatic increase in the generated photocurrent due to one or more of the following mechanisms: 1. Enhanced light trapping via Mie scattering by the nano- particles [3]; 2. Absorption enhancement via increased E-Field intensity in the semiconductor regions adjacent to the nano-particles, due to the excitation of Plasmons. [1][2][4],[5]; 3. Absorption enhancement in the underlying semiconductor substrate, via plasmonic coupling between adjacent nano-particles mediated by waveguide modes [6], [7]. A significant research effort has been invested in recent years to explore the various mechanism involved in the LSPR-enhancement of photo-generated current [5].

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In this preliminary study we have focused on the mechanism of LSPR-Related field enhancement in the vicinity of the nano particles embedded in silicon. The novelty in our research is the concept of using open metallic nano-shells embedded within the semiconductor medium to allow extraction of the generated photocurrent. The study was conducted by simulations using commercially available FDTD software (Fullwave™ by Rsoft).

Section 2 describes the simulation setup followed by the results given in section 3. The Result analysis and conclusions are detailed in sections 4 and 5.

2. METHOD

This study was conducted with a commercial Finite Difference Time Domain (FDTD) software RSoft FullWave™ supported by a suit of Python™ shell script written for implementing batch simulation and mass data analysis tasks. Fig. 1 shows the basic setup used for all simulations.

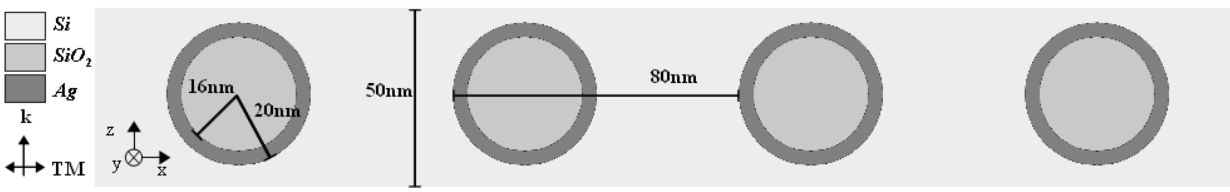

Fig. 1. Basic setup

The simulation setup was based on a single cell including one Ag Nano-Shell embedded in a Si substrate, 80nm wide and 50nm high. The simulation was set with periodic Perfect Matching Layer (PML) condition in the x axis, simulating an infinite lattice of nano structures. All simulations consisted of a complete or partial spectral scan of the spectrum between 300nm to 1000nm in 7.5nm steps. Each data point was made of a single FDTD simulation in which the transmitted and reflected power were calculated along with the absorption by Si. All measurements are expressed as a portion of source power. Following Prodan [8] and Tam [9] the first series of simulations researched the influence of tubes radii ratio on the intensity and location (wavelength wise) of plasmonic resonance. It consisted of a batch of 8 simulations in which the thickness of the shell was varied from 4nm to that of an entirely Ag filled tubes. At first we scanned the whole spectrum varying the shell thickness by 4nm steps. Then, in order to increase the resolution of our data, we added simulations between 4 to 8nm shell thicknesses in the range of 550 to 950nm where we identified a large variation in system's response. The second set of simulations aimed at studying the possibility of using the enhanced field created in the interface between Ag and SiO_2 to enhance the absorption in Si. It consisted of 3 simulations in which the nano Ag tubes were coated or "wrapped" by 0.5, 1.5 and 2nm SiO_2 shell. Following other works which suggested a strong dependence of the LSPR resonance on the shape and the surface to volume ratio of the particles (e.g Murray & Barnes [10]) the last set of simulations consisted of various tubes cross section shapes as detailed in Fig.2. The three closed forms (a, b, d) were chosen to explore geometrical features that may accentuate plasmonic resonance as well as enhance absorption.

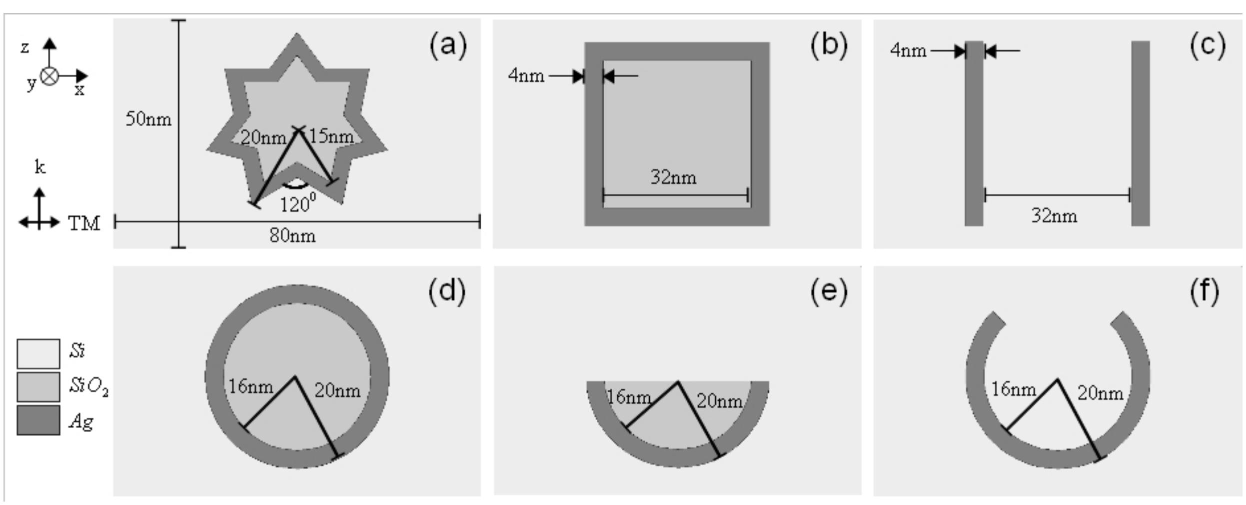

Fig. 2. Different tubes cross section. Semi circle and 270^0 circle (d, f) were tested twice once filled with Si and once with SiO_2.

The open forms (c, e, and f) represent nanoshell structures where the LSPR-enhanced photocurrent generated within the enclosing nano-shell can be potentially extracted to an outside circuitry.

All close nanoshell forms were filled with SiO_2 in order to reduce attenuation by Si absorption (whose related photocurrent generation cannot be extracted or used). Open forms (representing extractable photocurrent) however, were filled with either Si or SiO_2, with the results compared, as detailed below.

3. RESULTS

We examine the parameters impacting the absorption of light in a 50nm Si film embedded with nano Ag tubes. The first parameter to be studied was the thickness of the Ag shell. The second was the impact of tubes' cross section form on this absorption. Finally we tested the impact of the addition of a few nanometers SiO_2 wrapping layer around the tubes to examine the possibility of using the stronger LSPR-enhanced field generated in the SiO_2 (as compared to that of Si) for improving the absorption in Si.

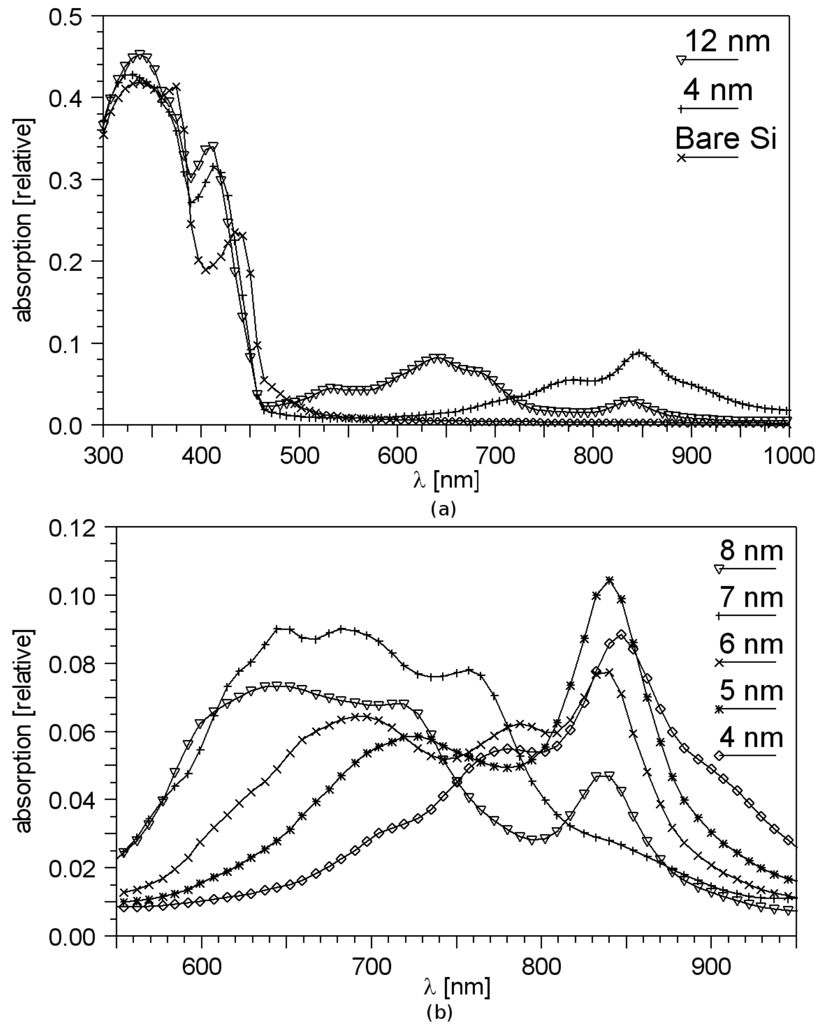

Fig. 3. Absorption by Si for 40nm diameter tubes with shell variation. (a) Shows two representative results for 12 nm and 4 nm compared to the absorption by bare Si. (b) Details of the shell thickness dependence of absorption, between 8nm to 4nm shell thickness.

Fig. 3 shows the results of studying shell thickness variations. Chart (a) shows the absorption by two representative shell thickness compared to the bare 50nm Si film. Results can be divided into two regions, from 300nm to 450nm and from 450nm to 1000nm. The lower region is characterized by an overall improvement that is slightly dependent on the shell thickness and therefore seems to be mostly impacted by tubes diameter. On the other hand the absorption at the longer wavelength region is highly dependent on the shell's thickness, as detailed in (b). Another important result is that although the maximum enhancement is shell thickness dependent, especially in the longer wavelength region, the overall improvement vs. a bare Si film is less dependent on it. Fig. 4 shows the result of the integrated absorption over two spectral regions; the first covering the whole spectrum and the second the 550-1000 region. (Values for 5-7nm shells were extrapolated from the 4 and 8nm simulation for wavelengths bellow 550nm and above 950nm).

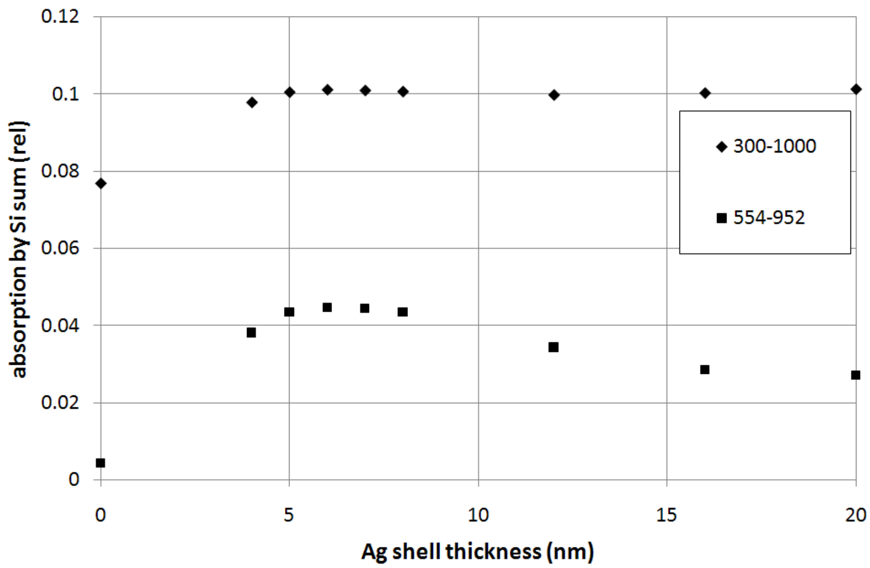

Fig. 4. Total absorption over two ranges. 0 shell thickness stands for bare Si and 20 shell thickness stands for whole tubes.

Fig. 5 shows the absorption by Si for tubes with approximately the same radii having each different cross section. Chart (a) shows results for open circular tubes cut at various angles. Open shapes in this case were alternately filled with either Si or SiO2. Chart (b) shows the results for the closed form cross sections. Fig. 6 compares the total absorption over the spectral range between 500nm to 1000nm acquired by the forms in Fig 5. Fig 7 shows Poynting vector magnitude for the fields generated by 4 of the cross section forms simulated, at the strongest resonance wavelength.

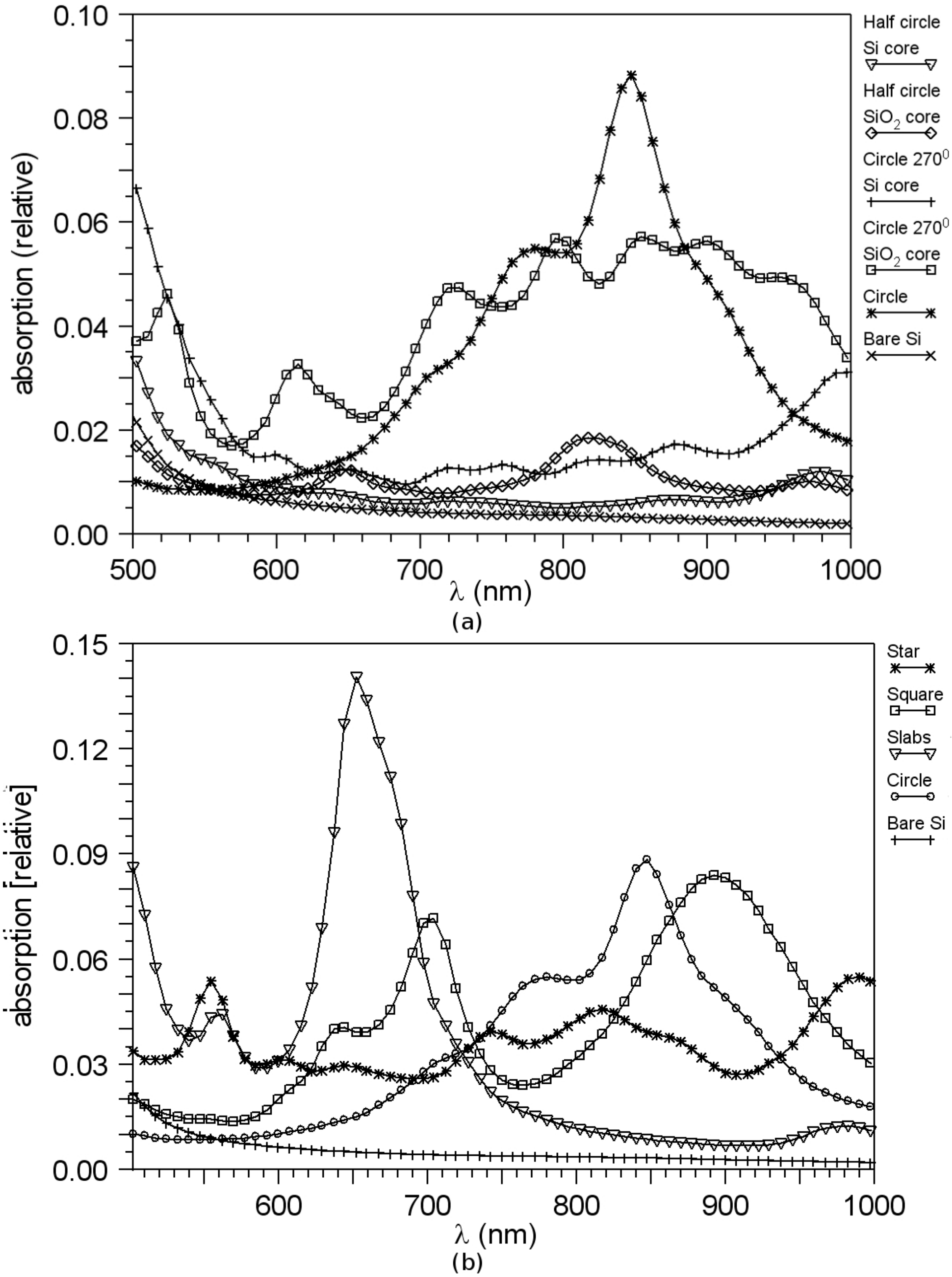

Fig. 5. Absorption by Si for 40nm diameter tubes with different cross sections (a) open circular with varying angle and core material (b) closed forms.

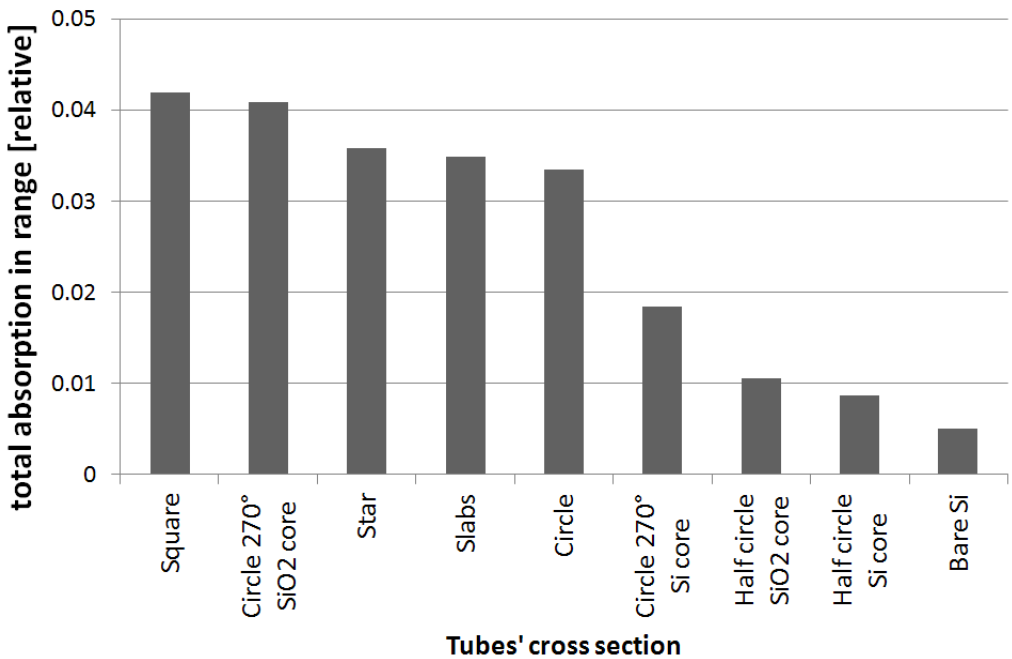

Fig. 6. total absorption of Si for tubes with different shapes in the 500-1000nm region.

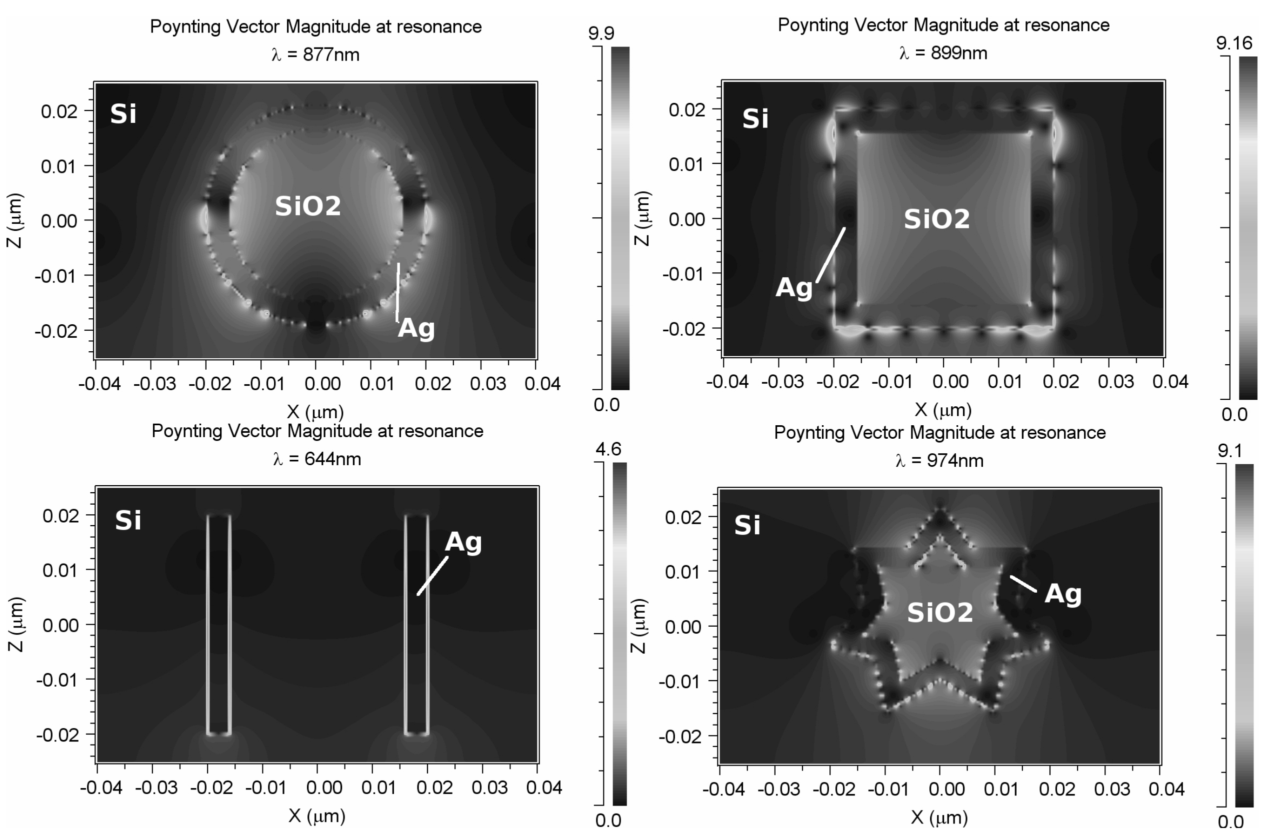

Fig. 7. Poynting vector magnitude at resonance wavelength for 4 cross sections form.

Finally in Fig. 8 we show the results for the experiment where we wrapped a close circular tubes with a SiO_2 thin layer. Here also the range can be divided to two. Below 450nm the addition of the SiO_2 layer had a small effect of enhancing the absorption in this region where the Si's natural absorption is high anyway. However in the longer wavelength range starting at 450nm, the addition of the wrapping layer adversely impacted the absorption enhancement and reduced it to values typical of bare Si. This behavior can be understood if one analyzes the field distribution across the sample displayed in Fig. 9. This chart shows the cross section at z=0 of the log of Poynting vector for a sample with a 1.5nm SiO_2 wrap and 930nm wavelength that is close to an Ag-SiO_2 plasmonic resonance. It can be seen that the enhance field generated at the interface between silver shell and the SiO_2 wrap first drop exponentially in SiO_2 as expected from a plasmonic field. Then it drops abruptly at the interface with Si (~6.5 times at the given example) to a value that is close to its normal value without resonance. Thus it's clear that the enhanced field does not have any influence on the absorption by Si. Furthermore the addition of the SiO_2 isolates the Si film from the silver particle and therefore extinguishes the enhanced absorption seen without the wrap. This important result need however to be considered in the construction of Si films with embedded Ag nano structure. Thus it suggests that the interface must be clear of any oxidation in order to permit maximal enhancement.

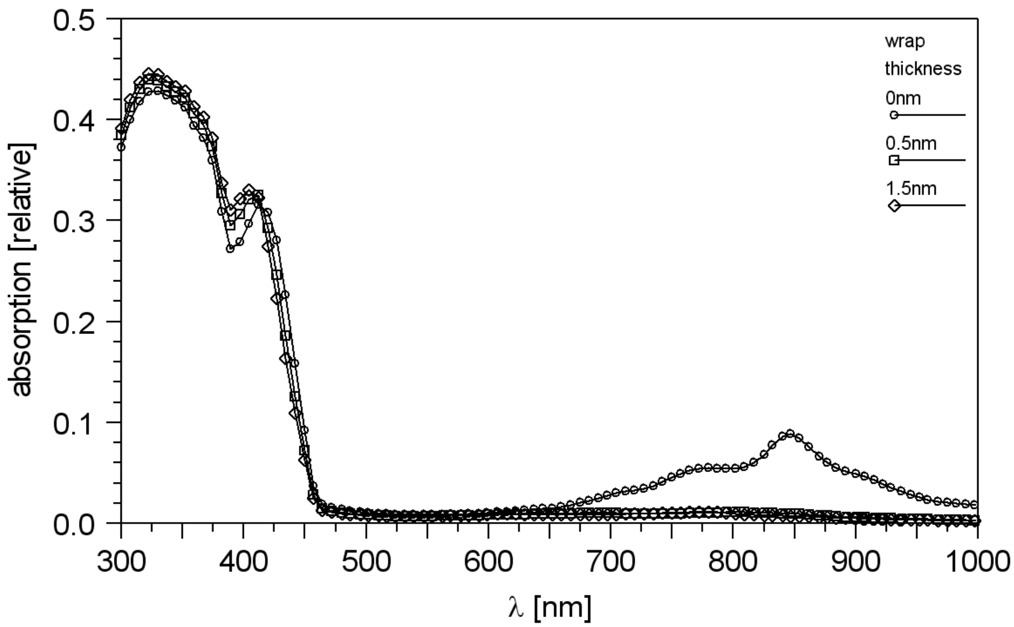

Fig. 8. Absorption vs. SiO_2 wrapping thickness.

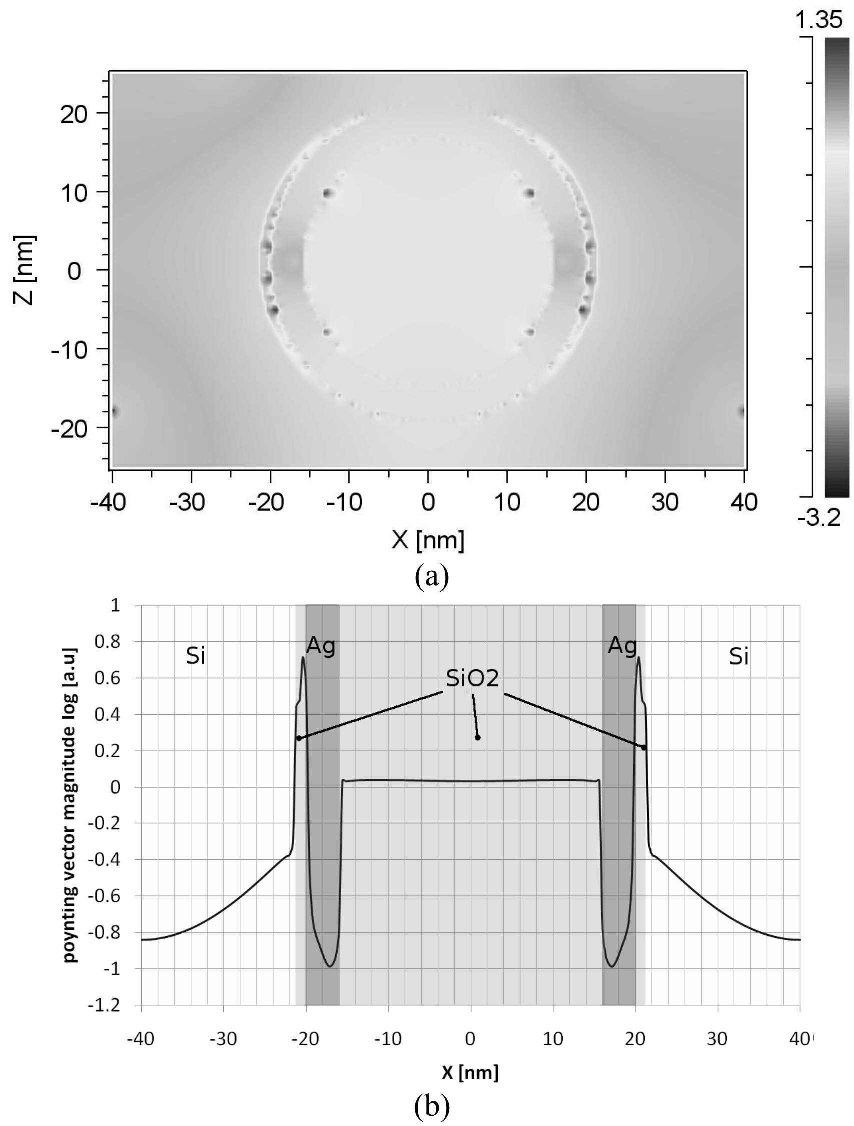

Fig. 9. Log of Poynting vector magnitude for a nano Ag tubes wrapped by a thin 1.5nm SiO_2 layer near to a resonance (Ag-SiO_2) wavelentgh of 930nm. (a) 2D map (b) Cross section at z=0.

4. ANALYSIS

We first confirmed the sensitivity of plasmonic resonance wavelength to the radii ratio of a concentric nano structure, having Si as its embedding material rather than pure dielectric (without losses) as already shown by others [8], [9]. As described in Fig.4, between 800% to 1000% in absorption enhancement can be achieved for almost the entire spectrum between 500nm and 1000nm with a suitable combination of shell thickness ranging from 4 to 8nm. Secondly we show the dependence of the plasmonic resonance location and absorption distribution in Ag tubes cross section. If we normalize the results to the effective metal thickness in each of the structures, the contribution of all cross section forms is approximately the same. However two exceptions to this were found, which are the two parallel slabs and the 270^0 circle filled with SiO_2 .Both of these structures show high total absorption although they contain relatively less metal then other structure. It should be noted that although nanoshells filled with Si core would be expected to induce a higher absorption rate than SiO2-filld cores, our results shows that closed circular tubes (filled with SiO2) give rise to the largest peak absorption along with the largest overall enhancement. Furthermore our results show that SiO_2 -filled open structures give both a higher local peak absorption and higher overall contribution. These results suggest that the principal role of the core's fill material is in determining the cavity's Quality factor and the related resonance intensity. Thus, the enhanced cavity effect by the SiO_2-fill, outweighs the added absorption of the Si-fill, resulting in SiO_2–filled nanoshell which outperforms Si-Filled nano shell in optimizing the overall Si-absorption. In addition, the results also show that an external SiO_2 wrap does not contribute to the absorption especially at wavelength in the region of interest, i.e. close to Si band gap. This suggests that the resonance enhancing SiO2 coating is outbalanced by its added thickness and the associated heavy decay of the Plasmon resonance before reaching the Si layer.

Finally, combining the results of the very short penetration depth of the enhancement field into the silicon substrate (Fig. 9b) ,with the significant absorption enhancement observed under these conditions, suggest that at least in this geometry of nano-shells embedded within the Silicon photo-substrate, the principal enhancement effect is that of near-Field-enhanced absorption rather than enhanced light scattering.

5. CONCLUSION

Enhancement of absorption in Silicon substrate using nanoshell-induced Local Surface Plasmon Resonance (LSPR), was studied using FDTD-based simulation. The 40 nm, tubular Ag nanoshells with shell thicknesses varying between 4nm and whole filled tubes were studied in the 300-1000nm region. The study also included various cross sectional shapes of nanoshells as well as open tubes shapes. The results indicate a very strong absorption enhancement of up to **10X** compared to that of a bare Si substrate. The spectral enhancement was found to be highly dependent on the thickness of the shells as well as on the cross-sectional shape of the tubular nanoshells.

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