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Modeling and calculation of light absorption in silicon/metal nanocomposites

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Abstract. Silicon thin films over a glass substrate has been considerate an economical and viable alternative for the photovoltaic industry. Implementation of this technology will contribute to preserve a clean environment helping to reach a sustainable future. Nevertheless, by their own nature, Silicon thin films present small light absorption, and its electrical energy conversion mechanisms is non ideal. The inclusions of metal nanoparticles in semiconductors can modify and improve the light absorption properties of these materials by surface plasmon interaction. It is well known that metal nanoparticles, deposited on the surface of Si-Solar cells, improve considerable the efficiency of the cell and it has been shown that there is a strong correlation between the surface plasmon excitation frequency and that of the exciting light. To study the light interactions on such material, we have developed a theoretical model that takes into account the incorporation of metallic nano-particles over Silicon thin films. We have obtained an analytical expression for the effective permittivity of the Semiconductor/Nano-particle system, ε_{eff}; using this result we have analyzed the light absorption process in the case of Silicon with two types of metallic inclusions.

1. Introduction

Improve the process efficiency for the conversion of light into electricity in semiconductor thin films would permit to situate the photovoltaic energy as the alternative energy source; this will be profitably and will be needed to promote the energy development and to contribute to the care of the environment. The crystalline silicon has emerged as a favourable material for applications with sunlight, but due its nature [1] and its low light absorption for wavelengths greater than 600 nm, its conversion capacity from light into electricity is not ideal. Recent research [2-5] has shown that the use of metallic nanoparticles (NPs) on the surface of solar cells produces an increase in photocurrent for wavelengths that coincide with the plasmonic wavelength of the nanoparticles, increasing the light scattering in silicon, and thus improving the light absorption in the material [5-7]. To study the effects of nanoparticles on Silicon, metallic nano-particulates, with desired composition and size, were manufactured [8] and they were embedded into the silicon thin film. Predicting the optical properties of nanocomposites created from optical materials is a recent research problem; there are some works proposing models to calculate the effective dielectric permittivity of a two component material [9 - 14].

H. Garcia *et al.* [15] reported a self-consistent technique to predict the plasmonic behaviour of nanocomposites, with multiple mixtures of metal (or alloy) nanoparticles, which is based on the fact

that for two components mixtures, the dielectric permittivity can be expressed through the Bergman-Milton formula [9, 10]. Using this in a self-consistent calculation, within the effective medium approximation, they calculated the effective permittivity of a composite of three components or ternary nanocomposites. The results obtained by H. Garcia et al. for optical density in a silicon oxide crystal were compared with experimental measurements obtained by other researchers [16-18]. It is to note that the method of mixtures predicts the position of the plasmon peaks and the changes occurred by varying the nanoparticle concentration. Although this method allows calculating the plasmon peaks and the system response as a function of the nano-particles concentration, it does not allow to obtain an analytical expression for the effective permittivity of the material. On the other hand, there is not known a theory to predict the behaviour shown by systems composed of more than two inclusions. This article proposes a model, which gets an analytical expression for the effective permittivity of the system Si + Nps with an arbitrary number of inclusions, and that allows to describe the experimentally observed behaviour of the optical density for the final mixture in a system comprised more than one inclusion.

2. Effective permittivity

The Semiconductors + Nps system consisting of a semiconductor matrix with N >>1 embedded spheres, with η different types of inclusions of radius a_i, where the subscript i refers to a particular type of inclusion. Considering the integral:

$$I_i = \frac{1}{V}\int(\vec{D}_i - \varepsilon_m\vec{E})dV \equiv \left\langle\vec{D}_i\right\rangle - \varepsilon_m\left\langle\vec{E}\right\rangle \qquad (1)$$

Where ε_m and ε_i are the permittivities of matrix and inclusion respectively, the integral (1) is different from zero only inside an inclusion [14]. The effective permittivity ε_{eff} is determined from equation (1) by the definition: <*D*>= ε_{eff}<*E*> for the electric displacement vector:

$$\left\langle\vec{D}\right\rangle = \varepsilon_{eff}\left\langle\vec{E}\right\rangle = \varepsilon_m\left\langle\vec{E}\right\rangle + I_i \qquad (2)$$

Besides, taking into account that *D*= ε_i*E* within an inclusion, the integral I_i becomes:

$$I_i = \frac{1}{V}\int(\varepsilon_i - \varepsilon_m)\vec{E}dV \qquad (3)$$

Where the integration is done on the volume of an inclusion of type i and gets to the result:

$$I_i = 3p_i\varepsilon_m\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m}\vec{E}_{loc} \qquad (4)$$

In this last expression it has been considerate that the electric field for spherical particles is given in terms of local field E_{Loc} [14, 19]. The average electric displacement <*D*> is obtained by taking into account the contribution of all η different types of inclusions, i.e.: considering the sum $I=\Sigma_i^\eta I_i$, which together with (2), allows to obtain the following relationship for the electric displacement vector:

$$\left\langle\vec{D}\right\rangle = \varepsilon_m\left\langle\vec{E}\right\rangle + \sum_i^\eta 3p_i\varepsilon_m\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m}\vec{E}_{loc} \qquad (5)$$

To calculate E_{Loc}, we make use of the Lorentz-Lorentz formula [20], in the form:

$$\vec{E}_{Loc} = \left\langle\vec{E}\right\rangle + \frac{4\pi}{3}\vec{P} \qquad (6)$$

where $<E>$ is the average field and P the polarization field of the particle. This last field is calculated using the approach proposed by R. Barrera *et al*. [21], where the relation between P and the average field $<E>$ is studied in the so called dipole approximation, considering that the electric field induced in each sphere has only a dipole character. That is valid provided that the electric field responsible for polarization of each sphere is virtually constant over the dimensions of the same, supposition which, on its turn, is only valid when the concentration of spheres is not very large.

On the other hand, the polarization field depends on the distance between spheres pairs, but as they present a random distribution, the calculations are a rather complicated problem. An approximate solution for this problem is developed in the framework of the Mean Field Theory, which assumes that the induced dipole moments $\{p_j\}$ could be approximated by the average dipole moment $p_j \approx P(R_j)/n(R_j)$, where $n(R_j)$ is the number density of spheres. Following this last treatment [21] and as: $\Sigma_i^\eta N_i = N$, it is obtained for the polarization field:

$$\vec{P}(\vec{R}) = \frac{3}{4\pi} \left[\left(\sum_i^\eta q_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \right)^{-1} - 1 \right]^{-1} \vec{E}(\vec{R}) \qquad (7)$$

Where $q_i \equiv n_i v_i$ is the volume concentration of i type inclusions and v_i the corresponding volume of the inclusion, and $\Sigma q_i + q_m = 1$. Combining equations (5), (6) and (7), after little algebra, it is obtained that the effective permittivity, for the system Semiconductor + Nps, with a η number of different types of inclusions, is given by:

$$\varepsilon_{eff} = \varepsilon_m + 3\varepsilon_m \left(\sum_i^\eta q_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \right) \left[1 + \left(\left(\sum_i^\eta q_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \right)^{-1} - 1 \right)^{-1} \right] \qquad (8)$$

3. Results

The effective permittivity for a system Semiconductor + Nps is shown in Equation (8) with number η of different types of inclusions. For the beginning considered a single inclusion, ie $\eta = 1$, the equation (8) becomes

$$\varepsilon_{eff} = \varepsilon_m + 3q\varepsilon_m \frac{\varepsilon_i - \varepsilon_m}{(\varepsilon_i + 2\varepsilon_m) - q(\varepsilon_i - \varepsilon_m)} \qquad (9)$$

That is the Garnett formula [11] giving the effective permittivity corrected for the contribution of the polarization fields, for a mixture of two components. As a particular result, we studied the case in which two types of metallic inclusions are embedded in the semiconductor matrix. Making $\eta = 2$ in (8) the effective permittivity takes the form:

$$\varepsilon_{eff} = \varepsilon_m + 3\varepsilon_m \left[\left(q_1 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} + q_2 \frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 + 2\varepsilon_m} \right)^{-1} - 1 \right]^{-1} \qquad (10)$$

In this equation, when $q_1 = 1$ and $q_2 = 0$ the Garnett formula (9), is obtained again. With the purpose to take into account the increased of the scattering due to the nano-particle size effects, we introduce a change in the imaginary part of permittivity of each metal, expressing the damping constant [22] as

$$\Gamma_{eff} = \Gamma_{bulk} + \frac{v_F}{2d} \qquad (11)$$

Where Γ_{bulk} is the inverse of the relaxation time for the electrons in the metal, v_F the speed of the electrons near the Fermi surface, and d the diameter of the nano-particle. The second term in (11) takes into account collisions of electrons with the metallic particles with spherical shape and also will take in account the correction for nano-particles with this geometry [23].

4. Comparison with experimental results

For testing the relation (10), the optical density of the system, which is proportional to the absorption of material, was compared with the results obtained by H. Garcia et al. [15] for a SiO_2 matrix with inclusions of Ag and Cu. This comparison is illustrated in Figure 1.
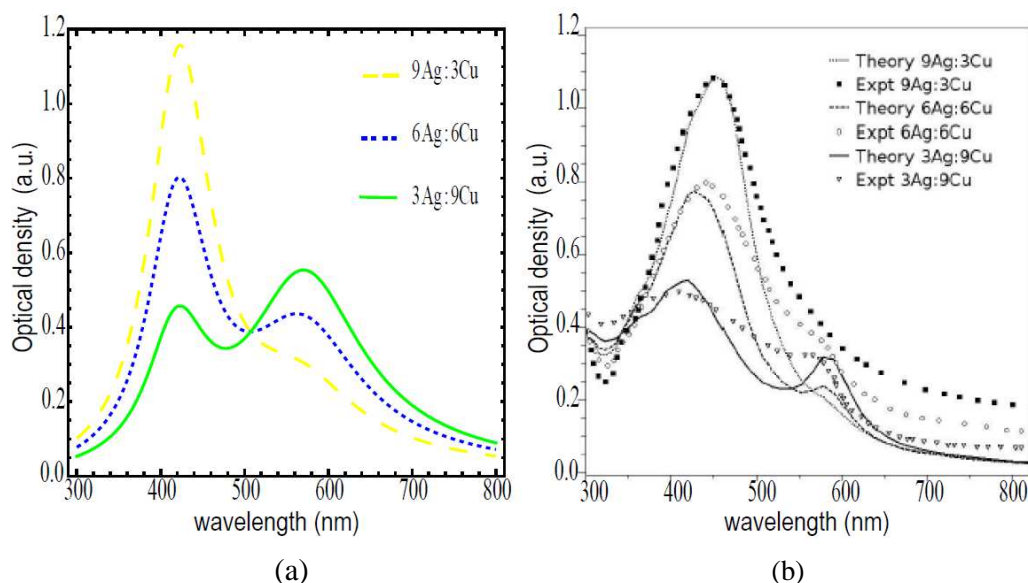

Figure 1: Optical density as a function of wavelength. (a) Obtained from equation (10). (b) Comparison of experimental results (points) and the theory of mixtures rules (lines) (Adapted from H. Garcia *et al.* [15]).

It can be seen that the general behavior observed in the SiO_2 matrix with inclusions of Ag and Cu is, in a good approximation, predicted by (10). Besides, it is clearly shown in Figure 1 that the resonances lay within the visible spectral range.

4.1. Absorption in Si with Ag and Cu inclusions

As a particular application, it was studied the case of absorption in a $Si+Nps$ system, which consists of a Si matrix with Ag and Cu inclusions. The optical density for this system has been calculated using equation (10) and plotted in Figure 2, for different inclusion densities: $9Ag$:$3Cu$, $6Ag$:$6Cu$ and $3Ag$:$9Cu$.
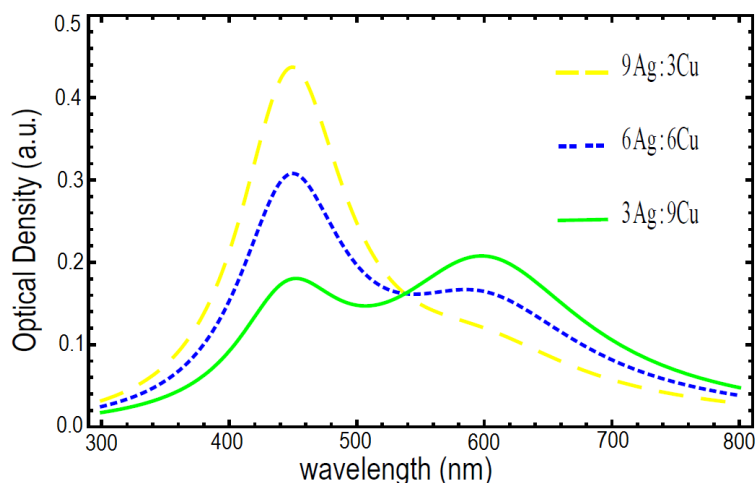
Figure 2: Optical density of Si for different densities of inclusions.

One can see the apparition of two resonances that is ascribe to *Cu* and *Ag* respectively in the range of the spectrum to visible light, which suggests that the absorption of system *Si+Nps* presented an increased light absorption with two resonant peaks for frequencies within the range of spectrum that is expected. Also can be see a strong dependence between the resonance amplitude and density of the inclusion respective, staying the resonances within the frequency range for the visible spectrum. It is clear that a higher density of inclusions leads to greater resonance value for each inclusion, besides the dependence of the amplitude with the type of nano-particle, to remark that the *Ag* has a greater resonance than *Cu* at the same density.

5. Conclusions

Using the dipole approximation and the mean field theory, an analytical expression for the effective permittivity of a *semiconductor+Nps* system with a general number of inclusions was obtained. This formula permits to study the light absorption process in the *semiconductor+Nps* system for the particular case of polycrystalline silicon matrix and two different types of inclusions (*Ag* and *Cu*). The inclusion of metallic nanoparticles in the matrix of polycrystalline silicon generates resonant peaks in the frequency range of the solar radiation spectrum, resulting in an enhancement of the light absorption by the material within the frequency range that is expected, in order to improve the efficiency of electricity production in a solar cell device. The amplitude of the resonance due each particle depends significantly on the density of the respective inclusion; the greater the density of inclusions than greater the generated resonance. The type of inclusion determines the value of the obtained amplitude, having as a particular case, that *Ag* has a greater resonance than *Cu* at the same density value.

References

[1]   Shockley W and Queisser H J 1961 *J. Appl. Phys.* **32** 510
[2]   Stuart H R and Hall D G 1998 *Applied Physics Letters* **73** 3815
[3]   Schaadt D M, Feng B and Yu E T 2005 *Appl. Phys. Lett.* **86** 063106
[4]   Pillai S, Catchpole K R, Trupke T and Green M A 2007 *J. Appl. Phys.* **101** 093105
[5]   Pillai S, Catchpole K R, Trupke T, Zhang G, Zhao J, and Green M A 2006 *Appl. Phys. Lett.* **88** 161102
[6]   Sundararaian S P, Grady N K, Mirin N and Halas N J 2008 *Nano Letters* **8** 624
[7]   Blackwood D J and Khoo S M 2010 *Solar Energy Materials & Solar Cells* **94** 1201–06

[8]   Burda C, Chen X, Narayanan R, and El-Sayed M 2005 *Chem. Rev.* **105** 1025-1102
[9]   Bergman D J 1980 *Phys. Rev. Lett.* **44** 1285
[10] Milton G W 1981 *J. Appl. Phys.* **52** 5286
[11] Garnett J C M 1904 *Trans. Royal Soc. London* CCIII 385
[12] Bruggeman D A G 1935 *Ann. Phys.* **24** 636
[13] Kohler W E and Papanicolaou G C 1981 *Multiple Scattering and Waves* ed P. L. Chow *et al* (North Holland, New York) pp 199-223
[14] Vinogradov A, Dorofeenko A and Zouhdi S 2008 *Phys.-Usp.* **51** 485-492
[15] García H, Trice J, Kalyanaraman R and Sureshkumar R. 2007 *Phys. Rev.* B **75** 045439
[16] Magruder R H III, Osborne D H Jr. and Zuhr R A 1994 *J. Non-Cryst. Sol.* **176** 299
[17] Battaglin G, Cattaruzza E, Gonella F, Mattei G, Mazzoldi P, Sada C, and Zhang X, 2000 *Nuc. Instr. Met. Phys. Res. B* **857** 166-167
[18] Moskovits M, Srnova-Sloufova I, and Vlckova B 2002 *J. Chem. Phys.* **116** 10435
[19] Landau L D and Lifshitz E M 1984 *Electrodynamics of Continuous Media* (Oxford: Pergamon Press)
[20] Lorrain P and Corson D 1972 *Campos y Ondas Electromagnéticas* (Selecciones Científicas)
[21] Adem E 2000 *Una ventana hacia la investigación en física* (Ediciones científicas Universitarias y FCE)
[22] Novotny L and Hecht B 2006 *Principles of Nano-Optics* (Cambridge University Press)
[23] Bohren C F and Huffman D R 1998 *Absorption and Scattering of Light by Small Particles* (Wiley Science Paperback Series)