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Opt. Data Process. Storage 2016; 2:1–6

Research Article

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J.F. Algorri, D. Poudereux, B. García-Cámara, V. Urruchi, J.M. Sánchez-Pena, R. Vergaz,
M.Caño-García, X. Quintana, M.A. Geday, and J.M. Otón*

Metal nanoparticles-PDMS nanocomposites for tunable optical filters and sensors

Abstract: The peculiar optical response of polydimethylsiloxane (PDMS) doped with metallic nanoparticles can be employed to develop optical sensing materials. These nanocomposites may work in an ample range of temperatures, showing good linearity and high sensitivity. Plasmon resonances of the metallic nanoparticles produce interesting effects on the optical response by affecting the effective refractive index of PDMS. The high resonant response leads to a number of different configurations of optical filters and phase devices whose resonant frequency depends on the chosen nanoparticle. Moreover, the wavelength can be tuned up by external manufacturing conditions such as nanoparticle size or fill factor, and by working parameters such as temperature. This work develops the theoretical background required for the design of these structures, and evaluates the adequate dimensional and doping ranges for device optimization.

Keywords: Optical sensing, plasmonic resonance, tunable optical filter, effective refractive index

*Corresponding Author: J.M. Otón: CEMDATIC, ETSI Telecomunicación, Universidad Politécnica de Madrid, Av. Complutense 30, E28040 Madrid, Spain, E-mail: jm.oton@upm.es
J.F. Algorri, B. Garcıa-Cámara, V. Urruchi, J.M. Sánchez-Pena, R. Vergaz: Electronic Technology Department, Carlos III University, Butarque 15, E28911 Leganés, Madrid, Spain, E-mail: brgarcia@ing,uc3m.es; vurruchi@ing.uc3m.es; jmpena@ing.uc3m.es; rvergaz@ing.uc3m.es; jalgorri@ing.uc3m.es
D. Poudereux, M.Caño-Garcıa, X. Quintana, M.A. Geday: CEMDATIC, ETSI Telecomunicación, Universidad Politécnica de Madrid, Av. Complutense 30, E28040 Madrid, Spain, E-mail: manuel.c@upm.es; x.quintana@upm.es; morten.geday@upm.es; jm.oton@upm.es; d.poudereux@upm.es

1 Introduction

Polydimethylsiloxane, also called PDMS or dimethicone, is the most widely used silicon-based organic polymer, especially in applications where optical or rheological properties of the materials are relevant. A mineral-organic polymer of the siloxane family, it belongs to a group of polymeric organosilicon compounds commonly referred as silicones [1]. It is specifically known for its unusual properties. PDMS is elastomeric and transparent at optical frequencies, shows low auto-fluorescence [2] and is considered biocompatible, hence its use in contact lenses. PDMS sticks tightly to glass or another PDMS layers yet remaining flexible. With some optimization, it is possible to mold structures of few nanometers [3], making it ideal to fill small cavities modifying their optical properties, for example in photonic fibers [4].

These remarkable properties have led to the proposal and development of an outstanding number of applications grounded on PDMS composites, and extended to many different areas: for example, tactile or pressure sensors based on capacitance variations [5, 6], microheaters obtained by external electric or magnetic driving of PDMS elements doped with metallic particles [7, 8] and biosensors in microfluidic systems, photonic crystals or micromembranes [9–11].

On the other hand, surface plasmon resonances of metallic nanoparticles (NPs) are well-known phenomena that have attracted much interest as soon as reliable procedures for NP manufacturing were developed [12]. NPs have been dispersed in a number of matrices giving rise to different effects and applications: for example, it has been demonstrated [13] that gold NPs dispersed in poly (methyl methacrylate) (PMMA) can be employed to create waveguides that may be used to develop optical couplers compatible with planar organic polymer photonics. Moreover, it has been shown that the scattering cross-section can be optimized for a given wavelength within an ample spectral range.

A number of works have reported the possibility to obtain homogeneous samples of colloid NPs in PDMS [14, 15].

NPs immersed in PDMS matrices have been used in developing optical microfluidic [16] and strain [17–20] sensors, as well as several biological-related applications such as biosensors [21], bio-analytical detection devices [22], and antibacterial-enhanced materials [23]. Recently, the tunability of plasmonic resonances of metallic NPs in PDMS has been shown up. The nanoparticle size and the fill factor affect considerably some parameters like absorption [24]. Static variations of uniaxial and biaxial strain applied to the composite lead to the same behavior [25]. Moreover, PDMS is known by its extraordinarily large and linear thermo-optic coefficient (dn/dT) [26]. Besides its obvious application to thermal sensors [27], this variation could be an excellent tool to control tunability of NP-PDMS composites. Nevertheless a full analysis of the thermo-optical properties of PDMS-doped mixtures has not been completed yet.

In this work, a thorough study of the thermo-optical response of PDMS doped with metallic NPs is carried out. The spectral position of plasmon resonances and their tunability range are formulated and solved numerically. The goal of the study is to pave the way to the design and fabrication of optimized devices tailored for specific applications.

The work has focused on silver nanoparticles, although its methods could be easily extended to other nanocomposites. Silver NPs are very common, present a sharp plasmon response and are compatible with PDMS. The effective refractive index of the composite present a high resonant response, due to the plasmon resonance of the Ag NPs, resulting in an important enhancement of light absorption. This effect can be extremely useful in phase-based designs using interferometric configurations such as Fabry–Pérot [28], Mach–Zehnder [29] or photonic crystal fibers [30]. Tunable spectral range with temperature variations is noticeable; NP size and fill factor, which considerably affect the tunability, are included in the calculations as well.

2 Theoretical background

In order to analyze the optical response of the mixture both refractive index and absorption are studied. The effective refractive index of the mixture is estimated by the effective medium theory. The absorption is studied through the analysis of the extinction cross section.

2.1 Refractive index. Effective medium theory

The effective refractive index of the PDMS doped with NP mixture can be explained through the Maxwell–Garnet effective medium theory described in ref. [31]. In the referenced work, the effective permittivity of the isotropic medium in combination with NPs is given by

$$\varepsilon_{av} = \varepsilon_m \left[1 + \frac{3f \left(\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right)}{1 - f \left(\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right)} \right] \qquad (1)$$

where ε_m is the electric permittivity of the PDMS, and ε is that of the Ag NPs; f is the volume fraction of NPs in the composite.

The quantum effects in nanometric particles inhibit the use of bulk properties. However, the electric permittivity of Ag NPs can be estimated through the Drude expression given by [32]

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$

where ω is the angular frequency, ω_p the Ag plasma frequency, ε_∞ a corrective constant that accounts for the background electron screening at high frequency, and γ the scattering frequency of the electron as it travels through the material. These parameters can be extracted from reference [33].

2.2 Attenuation coefficient

The absorption of the mixture can be studied considering the attenuation of a light beam crossing a sample. From a general point of view, the intensity of the light passing through a distance h of a dissipative medium is exponentially attenuated following [31]:

$$I_{(z=h)} = I_{(z=0)} \cdot e^{-\alpha_{ext} \cdot h} \qquad (2)$$

This attenuation is the result of both the absorption and the scattering of the beam into the medium. This is usually known as extinction. Due to the resonant behavior of NPs, which produces a large enhancement of both the scattering and the absorption, the extinction of the mixture will be mainly dominated by NP response. In this sense, the attenuation coefficient a_{ext} can be related to the extinction cross section (C_{ext}) in the following way

$$\alpha_{ext} = \Re \cdot C_{ext} \qquad (3)$$

where $\Re$ is the number of particles per volume unit. In addition, the extinction cross section can be obtained using
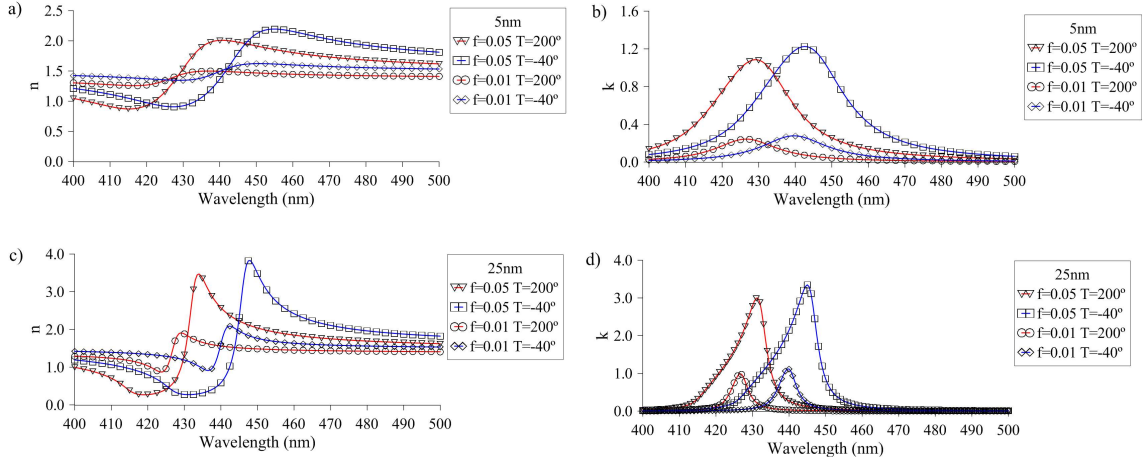
Figure 1: Effective refractive index of composites formed by PDMS and Ag NPs having fill factor 0.05 (red dashed line) and 0.01 (blue line). The real part of the index is shown in the two upper graphs, for NPs of 5 nm radius and 25 nm radius respectively. The two lower graphs are the corresponding imaginary parts of the same NPs.

the Mie theory [31].

$$C_{ext} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)Re(a_n + b_n) \qquad (4)$$

where a_n and b_n are the scattering Mie coefficients, depending on the properties of both the NP and the surrounding medium. k is the light wavenumber. The excitation of a resonance produces a peak in the spectral evolution of C_{ext}, at the resonant frequency.

3 Results and Discussion

We have checked the behavior of the system using the data sheet of a commercial PDMS, specifically Sylgard 184 of Dow Corning Corporation. This material should be operational over a temperature range of −45°C to 200°C for long periods of time [34]. Real and imaginary parts of the PDMS refractive index are calculated using the Sellmeier equation, whose coefficients have been experimentally determined in ref. [35]. PDMS absorption is almost zero at optical frequencies; therefore the imaginary part can be neglected [36]. The permittivity of the Ag NPs is estimated by using (2). Finally the refractive index of the mixture is estimated by using (1).

The real and imaginary components of PDMS refractive index doped with Ag NPs for different fill factors and NP sizes are shown in Figure 1. The plasmonic resonances of the NPs are affected by the temperature-dependent refractive index of PDMS. This effect produces remarkable changes in the effective refractive index of the composite. Two tunable parameters are possible. On the one hand,

the resonant wavelength of the refractive index response. The resonance peak can be tuned more than 15 nm in the whole temperature range. However, the lambda shift is not remarkably affected by the fill factor or the NP size. On the other hand, the refractive index amplitude can be tuned to maximize changes with temperature. For low fill factors and small NP radius, this effect is scarcely noticeable. For instance, considering a fill factor of 0.01 of Ag NPs with R = 5 nm, the real part of the refractive index (n) only ranges from 1.3 to 1.6 at −40°C. Increasing the concentration five times (0.05), the resonant effect increases. In this case, the real part of the refractive index ranges from 0.95 to 2.19 (at −40°C) around the resonance. For a specific wavelength (440 nm), the refractive index can be tuned from 1.36 to 2 for temperatures ranging from −40°C to 240°C. The imaginary part (k) has a behavior similar to the real part. This parameter indicates that absorption would be higher at the resonant wavelength range; moreover, it increases with concentration and NP size. As commented above, the tunable refractive index could be very useful in phase-based devices using interferometric configurations. Either of these configurations could be used to sense temperature, or could be tuned by temperature to generate another kind of devices.

Increasing the size increments the resonant peak as well. However, the increment in the NP radius has a different effect in the refractive index of the mixture. In this case, the peaks are more pronounced but have a smaller range of frequencies around the resonant frequency. In other words, the size increases the selectivity of the resonance. It is worth mentioning that even in this simple sys-

tem, the real part of the refractive index is near zero over a narrow wavelength range (f = 0.05 and R = 25 nm).

Another relevant device derived from this nanocomposite could be a tunable notch filter regulated by temperature or any other factor affecting the absorption peak position. The attenuation can be estimated following (2). Absorption depends on the number of particles per unit volume. If the NP size is increased and the fill factor is kept constant, the number of NPs on the sample decreases. When the NP size is small there are more NP per unit volume for the same fill factor. In (3), it has been observed that the effect of the number of NPs is greater than the effect of C_{ext}. The results of the output power ratio for different temperatures and fill factors are shown in Figure 2. A sample thickness of 10 μm has been considered.
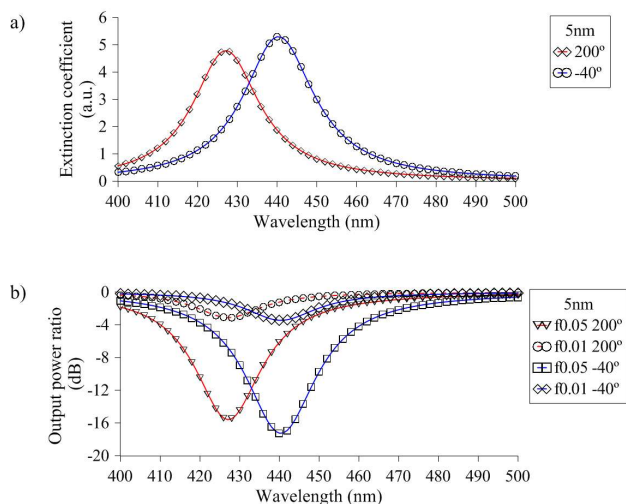

Figure 2: Extinction coefficient (a) and output power ratio (b) of composites formed by PDMS and Ag NPs. The fill factor is 0.05 (red continuous line) and 0.01 (blue line).

The plasmonic resonances of Ag NPs produce a high extinction cross section for a specific wavelength. The high thermo-optic coefficient of PDMS in combination with the tunability of the plasmonic resonances enhances the effect when the laser source has a peak emission in the same region as the resonant wavelength. In Figure 3 a laser source with a peak emission at 440 nm is used. PDMS doped with 5 nm Ag NP is considered. A sensitivity of $5.1{\cdot}10^{-2}$ dB/°C is obtained for fill factors of 0.05. The response is very linear in a broad range of temperatures.

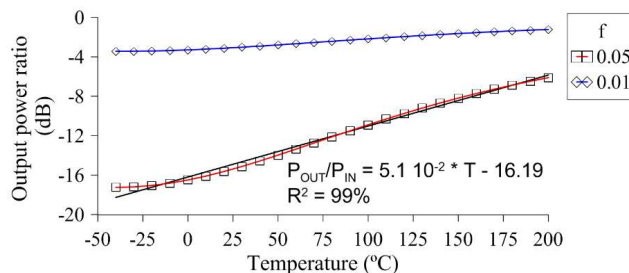**Figure 3:** Output power ratio of composite formed by PDMS and Ag NPs of R = 5 nm when a laser source of 440 nm is used; the sample has a thickness of 10 μm. The fill factor is 0.05 (red line) and 0.01 (blue line).

4 Conclusions

The optical response of PDMS doped with Ag NPs has been analyzed. Different fill factors and NP sizes were considered. For a low fill factor and NP size the effect of the resonance is low. Yet it could be applied to prepare schemes tunable by temperature in phase-based devices. Increasing the NP size enhances the selectivity of the resonance. The material could reveal useful in applications where a tunability of the refractive index is necessary.

A second approach is the use of the NP absorption. When a laser source centered in the region affected by the plasmonic resonances is used, a maximum variation of $5.2{\cdot}10^{-2}$ dB/°C is obtained for f = 0.05 and Ag NP of R = 5 nm. Besides the high sensitivity, the response curve of this material is remarkably linear. Several applications involving tunable fiber optic cavities regulated by temperature could be derived from this phenomenon. The broad range of working temperatures, the linearity and the high sensitivity of the system make this novel compound a very good candidate to devise applications as optical sensing element.

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