



# Functionally graded poly(dimethylsiloxane)/silver nanocomposites with tailored broadband optical absorption



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## ARTICLE INFO

Available online 28 November 2014

### Keywords:

Plasmonics  
Nanocomposites  
Silver  
PDMS  
Solar absorption

## ABSTRACT

In this work, we produce functionally graded nanocomposites consisting of silver (Ag) plasmonic nanoparticles (PNPs) supported in a poly(dimethylsiloxane) (PDMS) matrix. PDMS was selected due to its high optical transparency, nontoxicity and ease of use. The Ag PNPs were formed by annealing sputtered Ag ultra-thin films and were subsequently capped by a spin-coated PDMS layer. We investigate the factors that affect their plasmonic behavior, such as the PNP size, the annealing conditions and the surrounding environment. In order to achieve broadband absorption, we developed PDMS/Ag(PNPs) multilayers with graded PNP size. Thus, we demonstrate the significance of the stacking sequence of various plasmonic layers sandwiched between PDMS layers and its potential for tailoring the plasmonic response of multilayer structure. As a demonstration of this approach, we deposited a specially designed multilayer structure, whose optical extinction resembles the solar emission spectrum.

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## 1. Introduction

Nanocomposite films consisting of metal nanoparticles embedded into dielectric matrices have emerged as a significant category of engineering materials with applications in catalysis [1], optical storage of information [2–4], solar photothermal harvesting [5–7], decorative coatings [8–10], magnetism [11] and biocompatible surfaces [12–14]. Nanocomposites with embedded noble metal nanoparticles, which exhibit tunable optical properties due to the localized surface plasmon resonance (LSPR), have received recently particular scientific and technical interest. Usually, the dielectric matrices are either diamond like carbon [1,5,12–14] or ceramic [2,7–10], while reports of inorganic elastomer matrices, such as poly(dimethylsiloxane) (PDMS), are recent and rare [15–19]. In particular, PDMS combines a wide variety of assets, such as tuned flexibility or rigidity (depending on the curing conditions), optical transparency, chemical stability, environmental friendliness, hydrophobicity of its surface, tunable thermal conductivity, etc. In addition, PDMS-based nanocomposites can be produced using wet physical methods, such as spin coating, dip coating, drop casting, Dr Blade and brushing. Therefore, combining PDMS with noble metal plasmonic nanoparticles (PNPs) has the potential to revolutionize the industry of pigments and paints by implementing PNPs.

In this work, we present the concept of dispersing plasmonic silver (Ag) PNPs deposited by sputtering and then capped between PDMS layers, which are optically transparent and dielectric, in order to produce flexible plasmonic coatings with tailored optical absorption. The main asset of the proposed process is the versatility in producing graded and stratified Ag/PDMS structures with predesigned optical performance. We investigate the effect of annealing conditions, of the thickness of the Ag layers to their self organization. In addition, we show that small (<50 nm) Ag PNPs are self-capped by PDMS during thermal annealing. Finally, we demonstrate the significance of the stacking sequence of various plasmonic layers capped between PDMS layers and its potential for tailoring the plasmonic response of multilayer structure. As a demonstration of this approach, we deposited a specially designed multilayer structure, whose optical extinction resembles the solar emission spectrum.

## 2. Experimental details

For the PDMS production, we used the commercially available elastomer kit Sylgard 184 from Dow Corning. The PDMS kit consists of two components, the “base” and the “cross-linker.” The recommended weight mixture analogy base to cross-linker is 10:1. PDMS films were fabricated by manually mixing and stirring in a Petri dish the two components at the recommended ratio for 2 min. After stirring, the mixture was left to rest in order to remove the trapped air bubbles. The outgassed mixture was spin coated in a homemade spin-coater for constant rotation speed for 1 min onto a clean microscope slide. After spin

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coating, the samples were cured at 150 °C for 10 min in order to start the cross-linking process and obtain the elastomer film. The thicknesses of the elastomer films were lying in the range of 20 microns.

The deposition of Ag on Si wafers on glass slides and on PDMS took place in a miniature sputter coater system ( $P_{\text{bas}} = 3$  Pa) used for sample preparation for scanning electron microscopy. The high voltage was 1.5 kV; the Ar flow was controlled by a needle valve, in order to obtain a plasma current of 10 mA ( $P_w = 6$  Pa). Several samples we deposited for deposition times from 15 to 210 s. After deposition, the samples were annealed on a hotplate in air for 1 min at 250°. After annealing, another layer of PDMS film was spin-coated on top of the Ag deposited samples with the same process and a second annealing turn.

The optical properties of the samples were investigated in an ultraviolet–visible spectrophotometer (FR-Basic by Theta Metrisis) with Deuterium and Halogen lamps in the spectral range of 250 to 850 nm. Samples were measured in reflectance and transmittance modes, and reflectivity, transmittance and extinction values were acquired. The surface morphology of the samples was studied by scanning electron microscopy (SEM) at 5 kV and atomic force microscopy (AFM) (Ntegra Prima) in semicontact mode.

### 3. Results and discussion

As a starting point, and for having a reference of the formation of Ag PNPs by thermal annealing, we deposited Ag on rigid substrates such as Si wafers and glass slides. Fig. 1 shows two SEM images of a Ag sample deposited for 60 s on a Si wafer; Fig. 1a shows the as grown sample and Fig. 1b the same sample after annealing for 1 min at 250°. The image of the as grown sample reveals that the deposited Ag is uniform and forms either a continuous ultra-thin film or very small islands, which are smaller than the spatial resolution of SEM. The surface of the sample after the thermal annealing process is covered with Ag PNPs with broad size distribution. The annealing process melts the Ag on the as grown surface and gives the required energy to Ag atoms or clusters to diffuse on the surface and create stable larger PNPs [20,21].

The Ag PNPs size can be controlled by the actual amount of Ag deposited on the substrate. This is clearly demonstrated in Fig. 2, where SEM images of annealed samples deposited for various times on Si wafers are shown, along with the quantitative, statistical analysis of the corresponding images. In particular, the statistical analysis of the images shows that Ag deposition from 30 s to 180 s can produce PNPs with mean sizes ranging between 25 nm and 200 nm. The correlation between the PNP sizes and the deposition time, for the same annealing process, proves that the mean size of the Ag PNPs is related with the Ag amount deposited on the silicon surface. Greater (fewer) amount of Ag results to larger (smaller) PNPs. Also it is worth mentioning that above 90 s of Ag deposition, the PNPs have elongated shape and they are also partially interconnected.

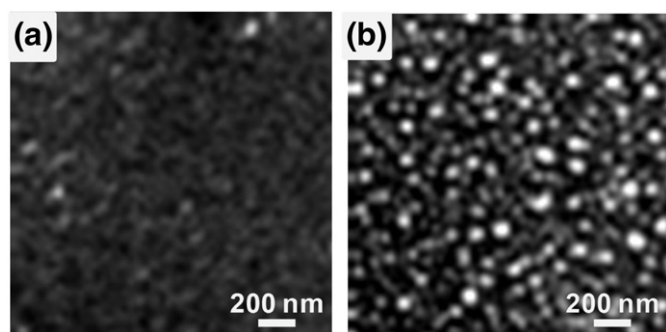


Fig. 1. SEM images of (a) as grown and (b) annealed Ag layer deposited for 60 s on a silicon wafer.

The formation of the Ag PNPs on the silicon surface is attributed to the bad wetting between Ag and silicon at low temperatures [22]. On the other hand, the wetting behavior of Ag on PDMS is unknown and the formation of Ag PNPs on PDMS and Si may substantially differ due to both the chemistry and hydrophobicity of the PDMS and Si surfaces (water contact angles 105° and 20°, respectively), as well as the viscoelastic vs. the rigid character of the PDMS elastomers and Si, respectively. In order to identify the behavior of the deposited Ag on the PDMS surface, we employed AFM topographic images after annealing since the PDMS is an insulator and the electron charging alters the imaging resolution of the SEM. Fig. 3 shows AFM topographic images of Ag deposition on PDMS samples for deposition times of 30 s, 60 s, 90 s and 120 s after the annealing process. The AFM images reveal the formation of Ag PNPs on the PDMS surface, as well. The PNPs cover evenly the PDMS surface for all deposition times. However, it is surprising that for the longer deposition times there is a clear bimodal distribution of Ag PNPs, which is strikingly different to what has been observed for Ag PNPs deposited on Si.

The mean size and the size distribution of the Ag PNPs are expected to greatly affect their LSPR spectral position. Indeed, Fig. 4a shows the optical extinction spectra of annealed samples with Ag deposited on PDMS (solid lines) and bare glass slides (dashed lines), for various deposition times (magenta, cyan, blue and red lines for 30, 60, 90 and 120 s, respectively). The optical extinction values have been extracted from optical transmittance measurements. The optical extinction spectra (Fig. 4a) reveal the presence of broad LSPR absorption peaks, which lie in the range of 450 to 650 nm for all samples. In both cases (Ag/PDMS and Ag/glass), there is a systematic redshift of LSPR with deposition time (Fig. 4b), which is associated with the Ag PNP sizes (Fig. 4c), as it is theoretically expected [23].

In Figs. 4b and c, the LSPR peak position and the average size of the Ag PNPs are plotted vs. the deposition time for PDMS (blue) and glass (red) substrates, respectively; the PNPs size has been determined by statistical analysis of the SEM/AFM images. In addition, we observe a cross over for samples deposited at times between 60 s and 90 s; in particular, for deposition times of 30 s and 60 s, the mean particle sizes are smaller for the samples deposited on glass, while for the longer deposition times the smaller mean size of particles and the shorter LSPR wavelengths are observed for particles formed on PDMS.

Figs. 5a and d show the extinction spectra of Ag deposited on PDMS samples for each processing stage for the production of the nanocomposites [as grown (black line), annealed (red line), capped with PDMS (blue line) and post-annealed (magenta line)] for the various Ag deposition times. None of the as grown samples exhibit an LSPR band because the sputter deposition of Ag at room temperature does not form any PNPs on the substrate. The annealing process for 1 min at 250° provides the required energy to the Ag to form PNPs; this is confirmed by the plasmon peak appearance (red lines) for every deposition time. The capping of the samples with a second PDMS layer increases the optical extinction values of the samples with an LSPR redshift, which is almost zero for 30 s Ag deposition, to over 200 nm for 120 s Ag deposition time. The redshift after capping by the second PDMS layer is theoretically expected due to the variations of the dielectric function of the surrounding medium [23] (the annealed sample consists of PNPs on top of the PDMS layer, while with the capping the nanoparticles are embedded into the new PDMS layer). Surprisingly, there is no redshift for the smallest Ag PNPs (30 nm, 30 s deposition) before and after capping providing strong indications that the PNPs are self-capped by PDMS during the annealing stage and before the capping stage, possibly by a sedimentation process. The Ag PNP sedimentation is more effective for smaller particles due to the minimized drag force of the viscous PDMS on the Ag spheres that is proportional to cross section of the particles. In order to clarify this, we performed analytical calculations using Mie's theory [24,25] considering perfect isolated spheres in a dielectric environment of a specific refractive index. We repeated the calculations for sphere sizes equal to all cases of Ag PNPs sizes presented in Fig. 4c, as

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