

# Plasma assisted deposition of Au/SiO<sub>2</sub> multi-layers as surface plasmon resonance-based red colored coatings

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# Plasma-Assisted Deposition of Au/SiO<sub>2</sub> Multi-layers as Surface Plasmon Resonance-Based Red-Colored Coatings

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**Abstract** In this work, the expanding thermal plasma chemical vapor deposition in combination with radio frequency magnetron sputtering is used to deposit dielectric/metal multi-layers with controlled size and density of nanoparticles. The multi-layer structure serves the purpose of increasing the nanoparticle number density, without changing the metal particle size, shape and the interparticle distance. The possibility of independently tuning and, therefore, controlling the nanoparticle size and number density allows developing surface plasmon resonance-based deep-colored coatings. The influence of the number of layers, metal surface area coverage, and thickness of the dielectric layer on the multi-layer nanostructure and on the developed color is presented here in detail. The nanoparticle size and distribution have been measured by transmission electron microscopy.

Rutherford back-scattering and infra-red transmission spectroscopy have been used to determine the metal surface coverage and the film chemistry, respectively. Optical properties of the nano-composite layers have been investigated by UV-VIS spectroscopy and exhibit an increase in amplitude of the plasmon absorption spectra at a fixed plasmon resonance frequency with an increase in the number of layers.

**Keywords** Multi-layer nanostructures · Dielectric/metal multi-layers · Surface plasmon resonance · Colored coatings · Hybrid ETP-CVD/sputtering

## Introduction

The combination of noble metal nanoparticles (NPs) with dielectric matrices has been the subject of research interest due to the several surface plasmon resonance (SPR)-based technological applications. SPR is the collective electron oscillation induced by the interaction of the electromagnetic radiation with a metal surface [1]. The resonance behavior (absorption maximum, full width at half maximum, and frequency) is strongly dependent on the nanoparticle characteristics (permittivity, shape, size, size distribution, and interparticle distance) and on the permittivity of the surrounding matrix [2–5]. In detail, the particle size affects the SPR mode due to confinement effects, as a result of the reduction of the mean free path of electrons, therefore, leading to an increase of the damping constant in the Drude model and, thus, of the SPR width [6–8]. In addition, the particle shape affects the width of the surface plasmon resonance [9] because of the scattering processes involved during optical excitation. The size distribution and interparticle distance are strongly related to the local field fluctuation and short-range near-field coupling, respectively

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[10, 11]. As a result of the dipole–dipole interaction between the nanoparticles, the distance between the neighboring nanoparticles plays a significant role on the surface plasmon band, which broadens and shifts to higher wavelengths as the interparticle distance decreases. Often, the interparticle interaction depends on the polarizability of the metal, particle size and number density, and metal surface area coverage of the NPs [12–14]. Therefore, it is considered very challenging to control the interparticle interaction independently from the particle size and metal surface area coverage.

In the last three decades, several techniques have been established to produce nano-composites, e.g., co-sputtering of the metal and the dielectric target from two different sources [15] or from a multi-component target consisting of the metal and the dielectric in a specific type of geometry [16, 17], alternated pulsed laser deposition [18], co-evaporation [19], hybrid processes combining sputtering, or evaporation of metals with simultaneous chemical vapor phase deposition of the dielectric layer [20]. However, due to the directionality of the physical vapor deposition techniques, preparation of nano-composites consisting of metallic NPs in a dielectric matrix with a controlled uniformity in shape, size, and density of NPs are still a challenge. Nevertheless, the tunability and control of the resonance condition by the change in microstructure is necessary and required in several technological applications, such as color filters [21], optical switching and optical limiting devices [22], optical biosensors [23], optical data storage [24], absorption elements of solar cells [25], photonic bandgap tuning [26], Bragg reflectors [27], and surface-enhanced Raman spectroscopy [28].

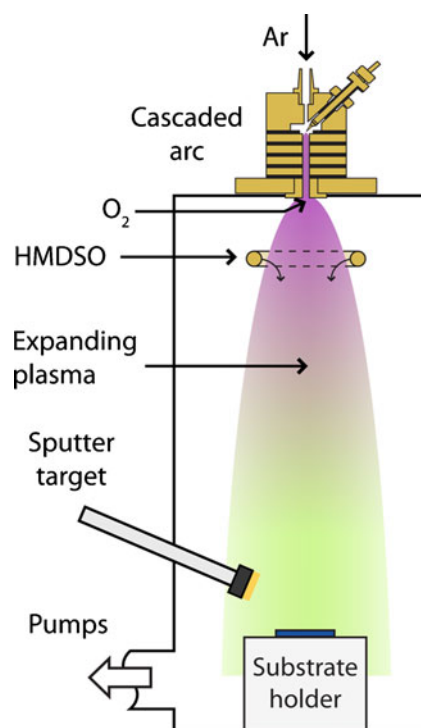
In previous works where homogeneous metal/dielectric composites have been synthesized by co-sputtering [29] and co-evaporation [19], the surface plasmon resonance resulted strongly related to the local metal volume fraction, also exhibiting a strong correlation with size, shape, and number density of NPs. Therefore, controlling the color intensity without a shift in position of the resonance peak is considered challenging when working with nano-composites. In this paper, the synthesis of metal/dielectric red-colored multi-layers for decorative applications is proposed and described, with the aim of independently controlling the size and the total number density of the metal NPs to enhance the color intensity.

## Experimental

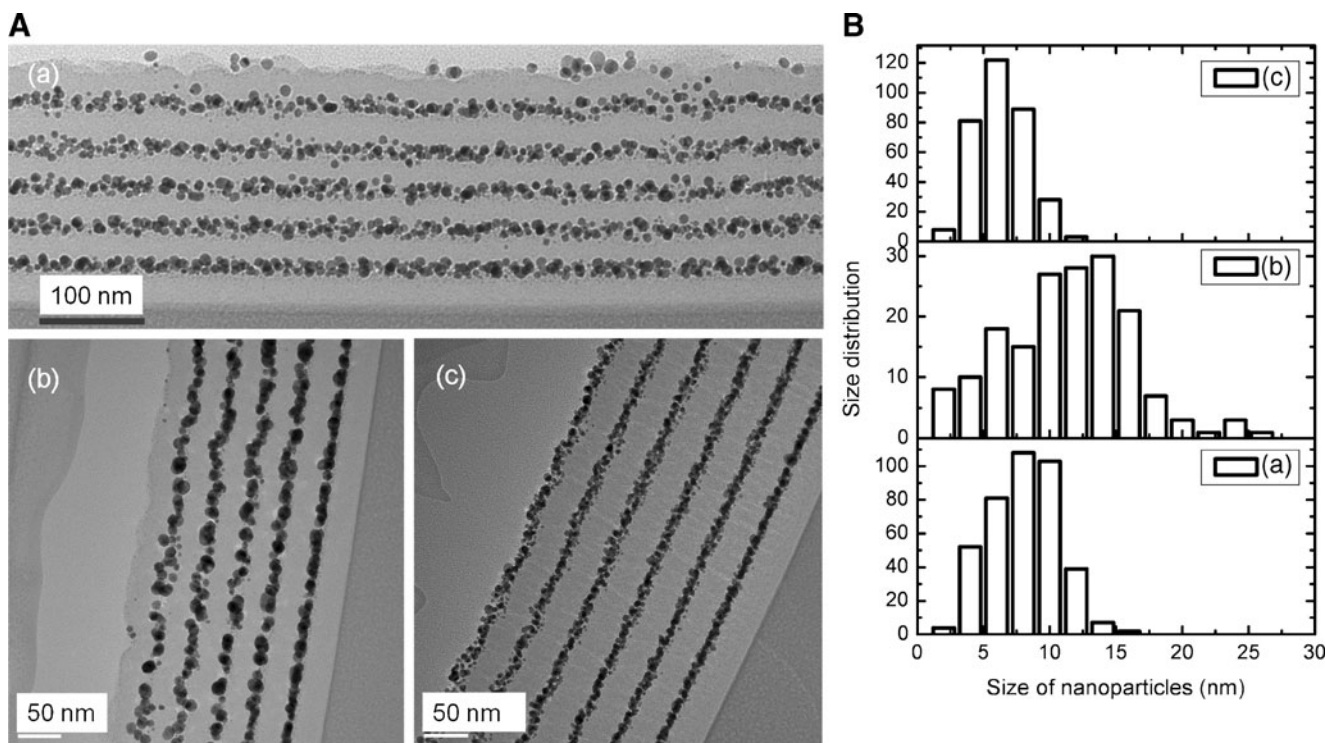
The feasibility of a PECVD (i.e., remote expanding thermal plasma, ETP) step followed by the ETP-assisted rf-magnetron sputtering technique for the deposition of Au nanoparticles on SiO<sub>2</sub> layers with a controlled shape, size,

and size distribution of the particles is demonstrated in our previous work [30]. Here, the same approach, shown in Fig. 1, is used to produce the metal/dielectric multi-layers. An Ar plasma ( $\Phi_{Ar}=70$  sccs) is generated in a cascaded arc operating at a current of 70 A and pressure of  $4.1 \times 10^4$  Pa. Due to the large difference in pressure between the cascaded arc housing and the deposition chamber (30 Pa), the Ar plasma expands supersonically through the nozzle in the deposition chamber. For the deposition of SiO<sub>2</sub>-like layers, O<sub>2</sub> ( $\Phi_{O_2}=5$  sccs) and hexamethyldisiloxane [(CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub> (HMDSO)] vapor ( $\Phi_{HMDSO}=0.46$  sccs) are injected into the chamber through the nozzle and a ring placed 5 cm below the nozzle, respectively. The film chemistry as well as the density and the optical properties of the SiO<sub>2</sub>-like layers are controlled by the precursors flow rate ratio ( $\Phi_{O_2}/\Phi_{HMDSO}$ ), the arc plasma parameters (Ar flow rate and arc current), and the substrate temperature during deposition [31–33]. The substrate is placed at a distance of 60 cm from the nozzle. The metal NPs were deposited using an ETP-assisted rf-powered magnetron head with a 2-in. gold target (Kurt J. Lesker Company, 99.99% purity) at a distance of 15 cm from the substrate and an angle of 75° from the substrate normal. The sputtering of the Au target was controlled by means of the RF-power, Ar flow rate, and arc current.

The films deposited on SiO<sub>2</sub>-coated copper grids were characterized by transmission electron microscope (TEM; Philips CM 30 operating at 300 keV) to determine the



**Fig. 1** The combined RF-magnetron sputtering and expanding thermal plasma-assisted chemical vapor deposition setup



**Fig. 2** Cross-sectional TEM images of Au/SiO<sub>2</sub> multi-layers deposited on a glass substrate (**A**) and size distribution (**B**) at constant plasma parameters and with the following deposition times for Au and substrate temperature, respectively: *a* 300 s, 300°C; *b* 400 s, 300°C, and *c* 300 s, 100°C

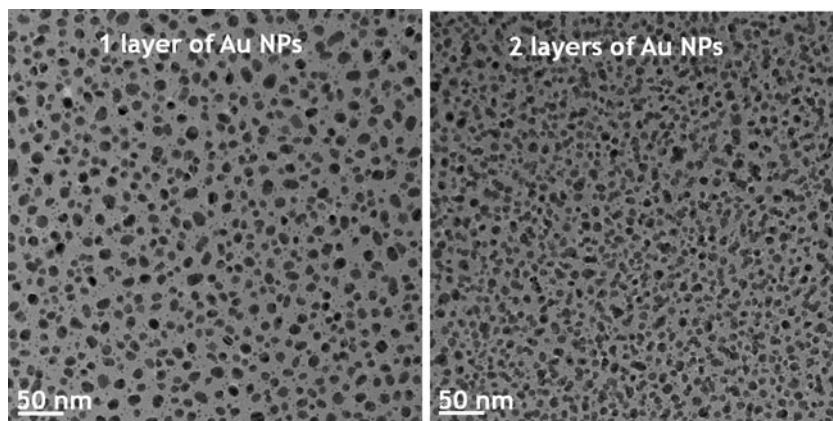
morphology of NPs. Rutherford back-scattering (RBS; 1.999 MeV 4He<sup>+</sup>) analyses were used to determine the surface density (mass thickness) of the Au layer on SiO<sub>2</sub>/c-Si substrate. Perkin–Elmer photospectrometer type Lambda 900 is used to determine the extinction spectra of the film deposited on SiO<sub>2</sub>/glass substrate.

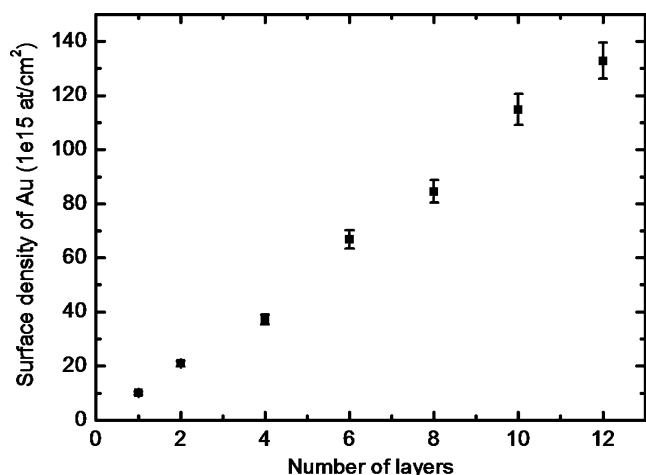
## Results and Discussion

Figure 2 (**A**) and (**B**) show the cross-sectional transmission electron micrographs of the Au/SiO<sub>2</sub> multi-layers and size

distribution deposited on a glass substrate as a function of the deposition time and substrate temperature, respectively. Figure 2a, b shows a particle size of 7±3 nm and 10±5 nm, respectively, suggesting the growth of larger NPs due to coalescence phenomena with longer deposition times. On the other hand, the lower substrate temperature during deposition is found to lead to a higher density of NP layers with smaller particle size (5±2 nm; see Fig. 2c). This is presumably related to the decrease in SiO<sub>2</sub> layer density as the substrate temperature decreases, as described in [31]. In this study, the refractive index of the SiO<sub>2</sub> layer deposited at lower substrate temperature (<200 °C) is lower than the

**Fig. 3** Topographic TEM images of Au nanoparticles prepared on carbon-coated copper grids for Au/SiO<sub>2</sub> and Au/SiO<sub>2</sub>/Au/SiO<sub>2</sub> deposited under the conditions of Fig. 2a

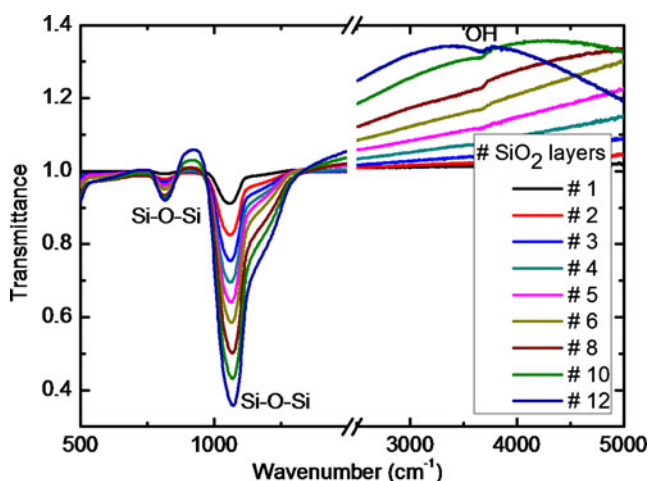




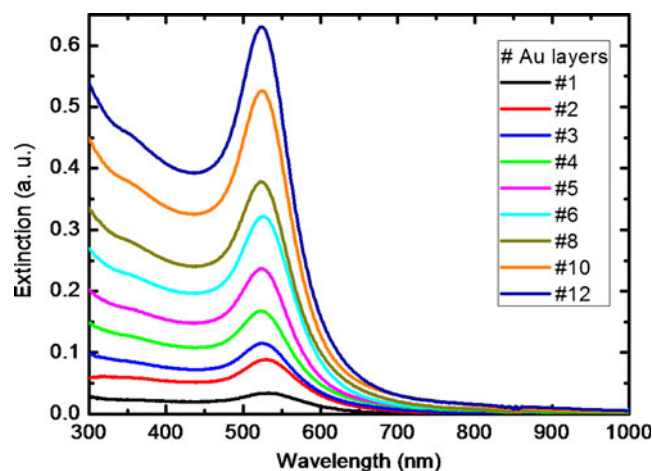
**Fig. 4** RBS analysis of the surface density of Au atoms as function of the number of layers

refractive index of the fused silica due to an increase of the porosity of the film matrix. Therefore, the surface porosity and, possibly, the presence of polar groups such as SiOH functionalities combined with higher surface roughness developed at low substrate temperatures, allow the NPs to grow on preferred sites, enhancing the density of NPs on the SiO<sub>2</sub> layer. The dependence of other parameters, such as the metal surface area coverage, number density, and the size of the NPs, from the deposition rate, deposition time, substrate temperature, and the chemistry and morphology of the dielectric layer, have been extensively discussed in [30], and detailed studies of the nucleation and growth of NPs on a dielectric layer [34] have been reported.

The multi-layer structure allows increasing the total number of Au NPs in the multi-layer structure by increasing the number of layers without undergoing a shape and size change due to particle aggregation. To verify the indepen-



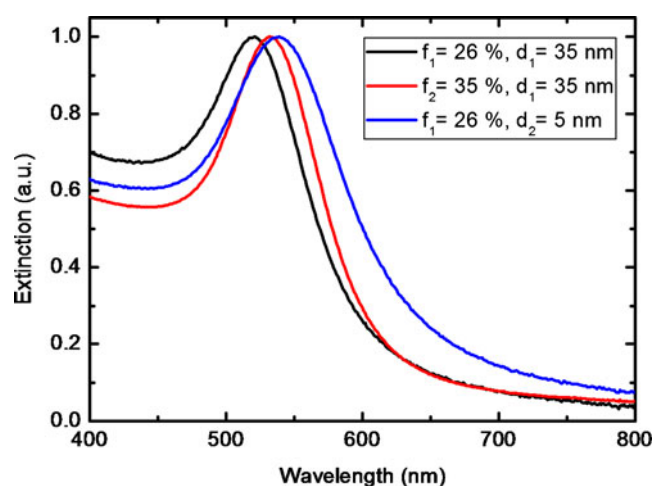
**Fig. 5** Infra-red transmission spectra of Au/SiO<sub>2</sub>-like multi-layers as function of the number of layers



**Fig. 6** Extinction spectra of the Au/SiO<sub>2</sub> multi-layer nanostructures for several numbers of Au/SiO<sub>2</sub> layers

dent control of size and the total number of NPs, topographical images of the Au/SiO<sub>2</sub>/substrate and Au/SiO<sub>2</sub>/Au/SiO<sub>2</sub>/substrate systems under condition (a) of Fig. 2 are shown in Fig. 3. It is observed that the total number density of the NPs increases with the number of layers at a similar size and size distribution, assuming the concentration of the particles in one layer is small enough and the probability of NPs to overlap with each other is negligible for the first two layers.

Moreover, RBS analyses have been carried out with two RBS detectors, one at scattering angle of 170° to determine the total Au content and one at 110° for better depth resolution in order to estimate the Au content of the individual layers. As a result, a linear relationship between the surface density of Au atoms and the number of layers is observed as shown in Fig. 4, which points out the linear



**Fig. 7** Extinction spectra of the Au/SiO<sub>2</sub> multi-layers at several metal surface area coverage ( $f$ ) values and thicknesses ( $d$ ) of the SiO<sub>2</sub> layer for a fixed number of layers ( $f_1=26.5\%$ ,  $f_2=35\%$ ,  $d_1=35$  nm, and  $d_2=5$  nm)

increase in the number density of NPs with the number of layers. A similar analysis allows determining the thickness of the individual SiO<sub>2</sub> layer to be 40 nm, based on the density of the SiO<sub>2</sub> ( $6.6 \cdot 10^{22}$  at/cm<sup>3</sup>). The thickness is confirmed also by TEM and spectroscopic ellipsometry. Based on the method described in [35], assuming that the NPs within a single layer are spherical and monodispersed, the interparticle distance in a layer can be calculated from the surface density (RBS) and average size of NPs (TEM) and obtained as 2.5 nm for the microstructure shown in Fig. 2a. The topographic TEM images show that, in reality, the distribution is not fully homogeneous. A direct measurement of the interparticle distance from these images was performed by measuring the interdistance of 40 particles with their five closest neighbors. This yields  $5 \pm 3$  and  $9 \pm 4$  nm for samples deposited in condition Fig. 2 (a) and (b), respectively.

In addition, infra-red transmission spectra, as shown in Fig. 5, exhibit only the several characteristic peaks associated with the SiO<sub>2</sub> matrix: the asymmetric ( $\approx 1,070$  cm<sup>-1</sup>) and symmetric stretching modes ( $\approx 800$  cm<sup>-1</sup>) of the oxygen atom with respect to the silicon atoms it is bridged to; their intensity increases with the number of layers. This indicates the absence of continuity among the NPs. The transmittance larger than 1 is attributed to the anti-reflection properties of the SiO<sub>2</sub> layer.

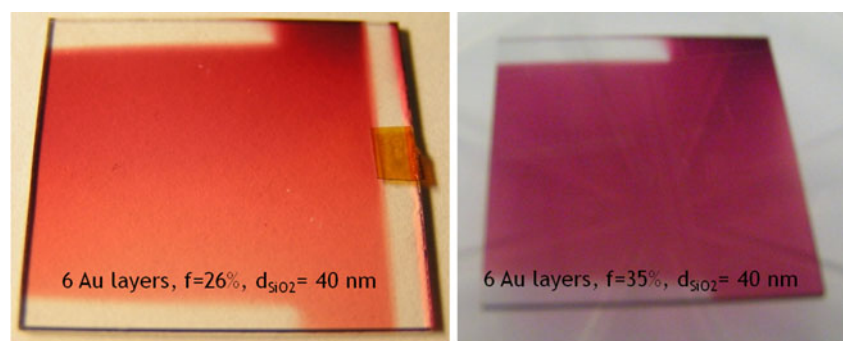
Recently, multi-layer structures consisting of Ag nanoparticles sandwiched between Si<sub>3</sub>N<sub>4</sub> dielectric layers deposited by double ion beam sputtering has been reported [36]. In our work, besides presenting a novel deposition technique for this specific application, proposes an approach to develop deep-colored coatings by suppressing a shift in position of the resonance peak. The thickness of the dielectric layer is optimized in order to avoid plasmon coupling between the metal NP layers in the multi-layer structure. Figure 6 shows the plasmonic behavior of the Au/SiO<sub>2</sub> multi-layers as function of the number of Au/SiO<sub>2</sub> layers measured by means of UV-vis spectroscopy (model Lambda 900 from Perkin–Elmer). The plasmon behavior exhibits a maximum in extinction which

increases with the number of layers, caused by the increase in the total number density of the particles. A change in the band width and resonance frequency is not observed as the size and size distribution of the Au NPs in each layer is controlled and kept constant. This approach allows producing a colored coating and intensifying the color with an increase in the number of particles. On the other hand, Fig. 7 shows a red shift of the plasmon resonance by increasing the metal surface area coverage on each layer and reducing the SiO<sub>2</sub> interlayer thickness. This is due to a deviation from the Mie plasmon resonance as a result of interparticle interaction and coupling in the SPR [37–39]. Taking into account that the SiO<sub>2</sub> interlayer is thick enough to avoid the SPR coupling between the Au layers, multi-layers are a valid solution to the production of strong colored coatings in which the color of the coating is virtually independent from the thickness of the film. Since the number density of the particles in each layer is small enough, interference effects are not observed in these layers and, therefore, the color of the film becomes independent of the viewing angle. Figure 8 shows the color appearance on a glass substrate for six layers of Au NPs separated by a SiO<sub>2</sub>-like layer (40 nm thick) at two different surface area coverage values in each layer.

## Conclusion

We have demonstrated the feasibility of the hybrid sputtering-ETP-CVD technique to deposit metallic NPs on dielectric surfaces. Multi-layers have been introduced as a solution for independent control of size and density of nanoparticles. The thickness of the dielectric layer sandwiched between two metal nanoparticle layers is an important parameter to optimize the plasmon resonance coupling; a 35 nm SiO<sub>2</sub> layer is found as an optimal thickness to avoid interaction between the Au NPs within two neighboring layers. In this regime, an increase in the number density of the nanoparticles at a constant size, and

**Fig. 8** Color appearance of the Au/SiO<sub>2</sub> multi-layers deposited on glass substrates under the experimental conditions reported in Fig. 7



size distribution allows suppressing a change of the plasmon frequency, while an enhancement in the maximum extinction is observed, which helps to produce an intense colored coating on arbitrary substrates.

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## References

- Kreibig U, Vollmer M (1995) "Optical properties of metal clusters", Springer Series in Materials Science, vol 25. Springer Verlag, Berlin-Heidelberg
- Noguez C (2007) *J Phys Chem C* 111:3806
- Luis M (2006) *Liz-Marzan. Langmuir* 22:32–41
- Lance Kelly K, Coronado E, Zhao LL, Schatz GC (2003) *J Phys Chem B* 107:668–677
- McFarland AD, McFarland AD (2003) *Nanoletters* 3:1057–1062
- Stephan L, El-Sayed MA (2003) *J Phys Chem B* 103:8410–8426
- Salerno M, Krenn JR, Lamprecht B, Schider G, Ditlbacher H, Féliidj N, Leitner A, Aussenegg FR (2002) *Opto-Electron Rev* 10:217–224
- Evanoff DD Jr, Chumanov G (2004) *J Phys Chem B* 108:13957–13962
- Naomi Halas (2005). *MRS BULLETIN*, 30: 362–367
- Ung T, Liz-Marza'n LM, Mulvaney Paul (2001) *J Phys Chem B* 105:3441–3452
- Rechberger W, Hohenau A, Leitner A, Krenn JR, Lamprecht B, Aussenegg FR (2003) *Opt Commun* 220:137–141
- Evanoff DD Jr, Chumanov G (2005) *Chemphyschem* 6:1221–1231
- Pinchuk A, von Plessen G, Kreibig Uwe (2004) *J Phys D Appl Phys* 37:3133–3119
- Wormeester H, Stefan Kooij E, Poelsema B (2008) *Phys Status Solidi* 205:756–763
- Schurmann U, Takele H, Zaporojtchenko V, Faupel F (2006) *Thin Solid Films* 515:801–804
- Mandal SK, Roy RK, Pal AK (2003) *J Phys D Appl Phys* 36:261–265
- Kim D-G, Koyama E, Tokuhisa H, Koshizaki N, Do Kim Y (2008) *Appl Phys A* 92:263–266
- Jun HS, Lee KS, Yoon SH, Lee TS, Kim H, Jeong JH, Cheong B, Kim DS, Cho KM, Kim WM (2006) *Phys Stat Sol A* 203(6):1211
- Takele H, Greve H, Pochstein C, Zaporojtchenko V, Faupel F (2006) *Nanotechnology* 17:3499–3505
- Martinu L, Poitras D, Vac J (2000) *Sci Technol A* 18(6):2619–2645
- Quinten M (2000) *Appl Phys B* 73:317–326
- Laura L (1997) Beecroft and Christopher K. Ober *Chem Mater* 9:1302–1317
- Haes AJ, Van Duyne RP, Am J (2002) *Chem Soc* 124:10596–10604
- Ditlbacher H, Krenn JR, Lamprecht B, Leitner A, Aussenegg FR (2000) *Opt lett* 25(8):563
- Catchpole KR, Polman A (2008) *Appl Phys Lett* 93:191113
- Bockstaller MR, Thomas EL (2003) *J Phys Chem B* 107:10017–10024
- Convertino A, Capobianchi A, Valentini A, Cirillo ENM (2003) *Adv Mater* 15:1103
- Nie Shuming, Shuming N, Emo SR (1997) *Science* 275:1102
- Boscarino D, Vomiero A, Mattei G, Quaranta A, Mazzoldi P, Della Mea G (2005) *J Vac Sci Technol B* 23:11
- Beyene HT, Tichelaar D, Peeters P, Kolev I, van de Sanden MCM, Creatore M (2010) *Plasma Process Polym* 7:657
- Creatore M, Cigal J-C, Kroesen GMW, van de Sanden MCM (2005) *Thin Solid Films* 484:104–112
- Hoex B, Peeters FJJ, Creatore M, Blauw M, Kessels WMM, van de Sanden MCM (2006) *J Vac Sci Technol A* 24:1823
- Creatore M, Barrell Y, Benedik J, van de Sanden MCM (2006) *Plasma Sources Sci Technol* 15:421
- Norbert Kaiser (2002), *Applied Optics* 41, 3053
- Tian Hao and Richard E. Riman, J. (2006) *Colloid and Interface Sciences* 297, 374,
- Lantiat D, Toudert J, Babonneau D, Camelio S, Tromas C, Simonot L (2007) *Rev Adv Mater Sci* 15:150
- Sancho-Parramon J (2009) *Nanotechnology* 20:235706
- Toudert J, Babonneau D, Simonot L, Camelio S, Girardeau T (2008) *Nanotechnology* 19:125709
- Maria L (2009) *Protopapa. Appl Opt* 48:778–785