Gradient silver nanoparticle layers in absorbing coatings—experimental study

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Metal island films show a characteristic absorption peak related to the surface plasmon resonance of free electrons. This kind of film can be used in absorbing coatings, together with dielectric layers. Such absorbing multilayer coatings, with and without the gradient of the silver mass thickness in metal island films throughout the coating, have been deposited by electron beam evaporation. It is shown experimentally that coatings with a gradient in the mass thickness of silver nanoparticles have higher absorption than equivalent nongradient coatings with the same total mass thickness of silver nanoparticles. © 2011 Optical Society of America

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1. Introduction

Metal grows as islands, rather than as a continuous film, when a small mass thickness is deposited onto a dielectric substrate. Thus, metal nanoparticles are obtained. Metal nanoparticles attract a lot of interest due to the surface plasmon resonance (SPR) of the free electrons, showing strong absorption at specific wavelengths that depend on the particle size, shape, and spatial distribution [1]. They are used in selective absorbers, optical polarizers, and data storage [2–4], or in chemical and biological sensing and surface enhanced spectroscopy [5,6]. Combining two metals, in the shape of an alloy or core–shell nanoparticles, it is possible to shift the absorption peak in an even wider range of wavelengths than when using one metal only [7]. The position of the absorption peak of the SPR depends also on the dielectric constant of the surrounding media [8]. Thus, embedding metal nanoparticles in dielectric multilayer coatings enables tailoring of the optical properties of multilayer systems.

Highly absorbing coatings can be obtained by using alternate dielectric/metal nanoparticle films, with the dielectric films being quarter-wave layers for the SPR wavelength. For these coatings, it has been suggested that the gradient decrease of the nanoparticle size or concentration toward the ambient suppresses light reflection and enhances broadband absorption over the visible range. All together, such coatings work not only on a principle of material absorptance, but also on interference. To obtain a lower reflectance R and higher absorptance A than in a nongradient system composed of identical nanoparticle layers, it is necessary to fulfill some conditions [2]. First, the reflectance should increase at each next nanoparticle layer from the ambient toward the substrate, while absorptances should decrease or be comparable. At the same time, the absolute value of the difference of the reflectances at successive layers should be bigger than the absolute value of the difference of absorptances. However, as the consequence of high reflectance of the layer next to the substrate, the absorptance with the back-side light incidence (Abs) is worsened in comparison to equivalent nongradient systems.

In reality, the gradient decrease of nanoparticle size or concentration, as theoretically studied in [2], cannot be obtained independently using standard techniques for the deposition of thin films. In order to confirm the described design principle

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experimentally, we have fabricated corresponding nongradient and gradient systems, consisting of silver metal island films in the SiO_2 matrix and satisfying the conditions for reflectance and absorptance. We have also proposed the improvement for the case of back-side light incidence.

2. Experimental

A multilayer structure of metal clusters embedded in a dielectric matrix was prepared by the sequential electron beam evaporation of Ag and SiO_2 at 1 mm thick BK7 glass substrates. The layer mass thickness was controlled by a quartz crystal monitor. We wanted to keep the total thickness of the metal low enough to have a measurable transmittance to be able to compare it with the reflectance and more easily notice fine differences between the absorptance peaks of different samples. The deposited mass thickness of Ag was in the range of 3–12 nm, leading to the formation of nanoparticle layers due to the islandlike growth of metals on the dielectric surfaces [1]. Deposition rates were around 1 Å/s for Ag and 10 Å/s for SiO_2. The substrates were preheated to 220 °C to enhance island growth [9].

In order to provide the same substrate for the growth of each Ag layer, the first layer deposited on the substrate is SiO_2. The last layer toward the air is also SiO_2. The mass thickness of all SiO_2 layers in the coating is 78 nm. However, because the dielectric at first fills the space between the Ag nanoparticles, the expected thickness of the grown SiO_2 layer corresponds to approximately 73 nm, which is quarter-wave for 420 nm. The samples in this study are distinguished by the mass thickness of Ag layers—the first number being the thickness in nanometers of the nanoparticle layer closest to the substrate.

The measurements of the optical performance of the samples at normal incidence were done by a PerkinElmer Lambda 25 spectrophotometer. Reflectance and transmittance measurements were performed in the range of 300–1100 nm, each 1 nm. The measurements of reflectance and transmittance at nonnormal incidence were done with a Woollam V-VASE ellipsometer in the same spectral range as with the spectrophotometer.

3. Results and Discussion

Figure 1 presents the absorptance and reflectance of $SiO_2/Ag/SiO_2$ coatings with 4, 7, and 12 nm of Ag mass thickness. These mass thicknesses correspond to particle diameters of 10–20 nm, with interparticle distances of 20–50 nm and are equivalent to layers with metal of the volume fraction 20%–35% [9]. The optical properties of the samples are dominated by the SPR of Ag particles: the absorptance has a maximum at the SPR peak position. The maximum shifts are in the range of 431–465 nm for the deposited mass thicknesses of 4–12 nm. At these wavelengths, the reflectance has a minimum due to the interference effects. The SPR is redshifted, broader, and more intense for Ag layers with a higher mass thickness, which can be related to the increase of the ellipticity of the nanoparticle shape and of the electromagnetic coupling between particles [1].

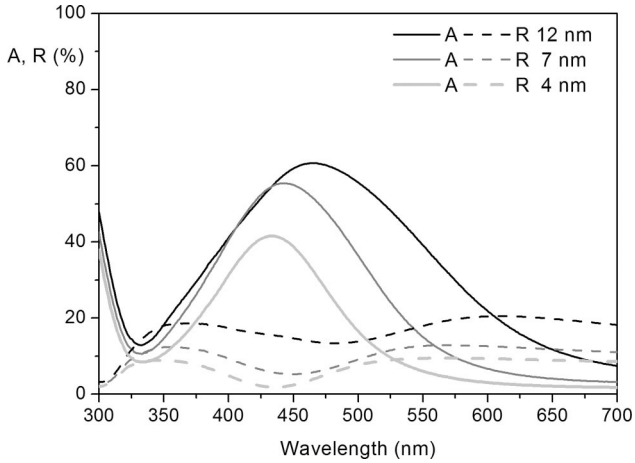

Fig. 1. Absorptance and reflectance of the samples with 4, 7, and 12 nm of Ag.

We show in Fig. 2 that the absorptances of the samples with 7 and 12 nm of Ag are comparable, in the range of 400 to 450 nm, where the SiO_2 makes quarter-wave layers, while the reflectances differ significantly in comparison to the difference of the absorptances. Therefore, this combination of layers is a good candidate for the gradient system. On the contrary, samples with 4 and 7 nm are not a good combination because the difference of the absorptances is bigger than the difference of the reflectances.

The absorptance measured for the light incidence from the coated side (A) and back side (Abs) of the samples containing two layers of Ag (i.e., $SiO_2/Ag/SiO_2/Ag/SiO_2$) $7+7$, $12+12$, and gradient $12+7$ nm of Ag, are shown in Fig. 3. It must be taken into account that Abs is limited by the reflectivity of the bare substrate side. It is confirmed that the gradient coating has a higher absorptance than the two nongradient coatings, although the total Ag mass

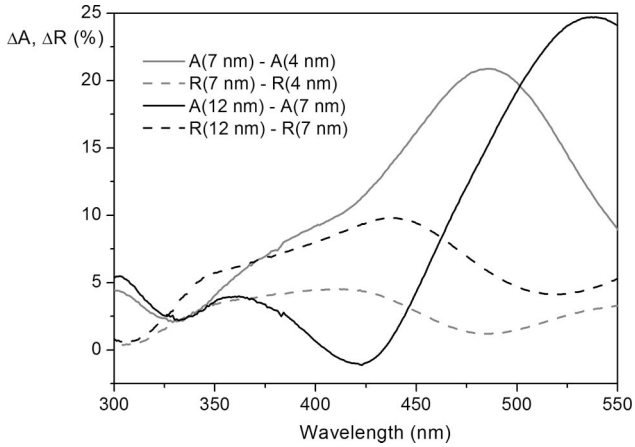

Fig. 2. Difference of absorptance and reflectance of the samples with 4, 7, and 12 nm of Ag shows that the last two make the combination that satisfies the condition for absorption enhancement in the range of 400–450 nm.

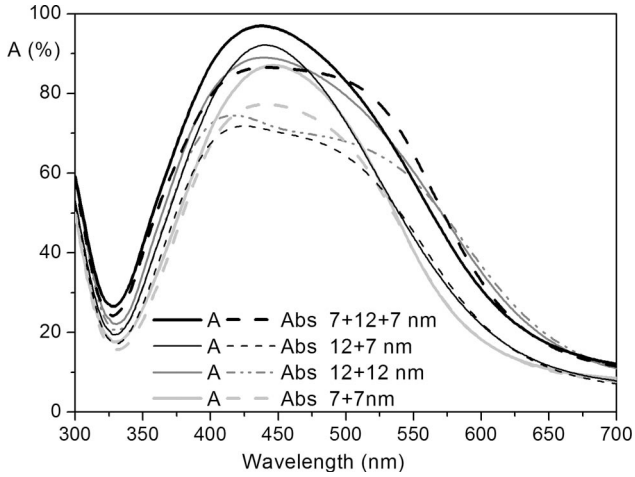

Fig. 3. Absorptance measured from both sides of the samples shows that the gradient system has higher A than nongradient systems, but lower Abs. The symmetric gradient system reduces the difference between A and Abs, compared to the simple gradient system.

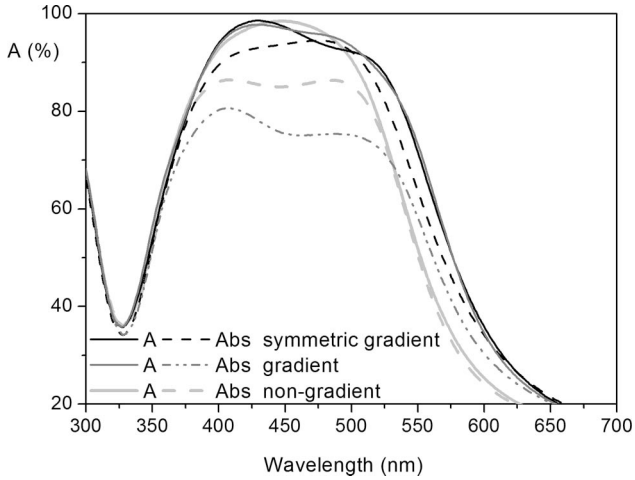

Fig. 4. Absorptance measured from both sides of the samples with the same total Ag mass thickness shows improvement of Abs for the symmetric gradient, compared to the nongradient system and simple gradient. Gradient systems have a broader absorption peak than nongradient systems.

thickness is lower. However, the Abs in the case of the gradient coating is worsened due to higher reflectance of the light at the layer of 12 nm than at the layer of 7 nm (compare Abs curves of samples $7+7$ nm, $12+12$ nm, and $12+7$ nm; see Fig. 3). In the case of high enough absorption in the first/second half of the coating, there is no light transmitted further. Thus, one-half of the coating is not affected with the other half, and antireflectance can be achieved from both sides using a symmetric structure. Therefore, we have made a symmetric gradient of three Ag layers $7+12+7$ nm, also shown in Fig. 3. This sample shows the reduced difference of A and Abs, compared with the difference in the simple gradient system.

In order to compare the performance of the systems with the same total Ag mass thickness, three coatings with five Ag layers, i.e., $(SiO_2/Ag)^5/SiO_2$, have been prepared and measured: a nongradient sample with five Ag layers of 7 nm, a gradient with Ag mass thickness of $11+9+7+5+3$ nm, and a symmetric gradient with an Ag mass thickness of $4+7.5+12+7.5+4$ nm. In Fig. 4 we show that gradient systems have an A peak comparable in intensity and wider than that of nongradient systems. Comparing Abs, it is clear that the symmetric gradient has superior performance than the other two samples. However, the condition for enhanced absorption is not obeyed between all the layers in the gradient (layers with 3 and 5 nm and layers with 5 and 7 nm) and symmetric gradient (layers with 4 and 7.5 nm) samples. The condition remains fulfilled between the three thickest films in each of the samples, having equal total metal island film thicknesses in both structures. The function of the thinner layers (that are breaking the rule) is to minimize reflectance at the first layer from ambient or substrate even more, making a sort of impedance matching, like gradient antireflection coatings do. So, although the condition for enhanced absorption is not obeyed, the absorptance of the coating is improved. Therefore, we recommend starting the gradient with thinner layers. Introduction of these thin layers also broadens the absorptance peak.

Figure 5 presents how the performance of the absorption peak changes with the angle of the light incidence for the case of the symmetric gradient coating. It is possible to see that the position of the absorption peak remains practically unchanged for the angles of incidence as high as 60°. The intensity of the peak decreases slightly, and it is reduced to 70% at the angle 75°. Because the absorption peak position is the property related to the resonance of surface plasmons of free electrons, it does not shift in wavelength with change of the incidence angle. However, the performance is disturbed at large angles. The reason for this comes mainly from interference in the dielectric coatings that is sensitive to the angle of incidence.

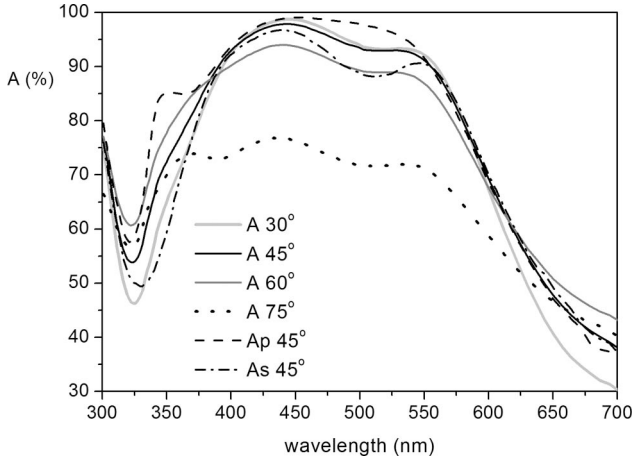

Fig. 5. Dependence of the symmetric gradient absorptance peak on the incidence angle. For the angle of incidence 45°, measurements for s and p polarization are shown as well.

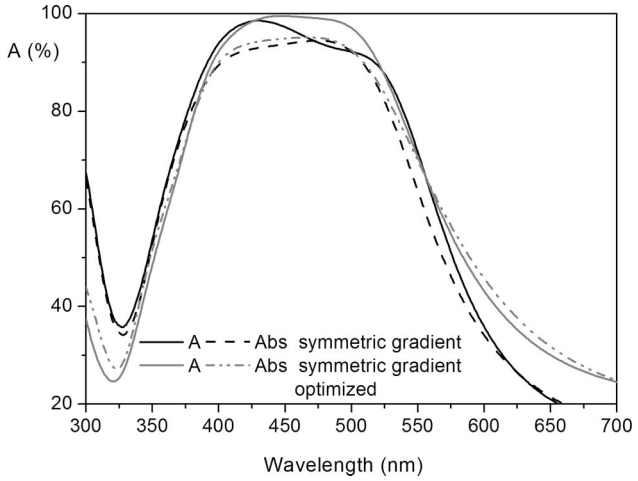

Fig. 6. Optimization of the thickness of the dielectric layers improves the performance of the symmetric gradient coating, for both cases: front- and back-side incidence.

The peaks of both gradient samples have a dip around 480 nm. This is related to the condition for enhanced absorption between thin layers that is most strongly broken around 480 nm (see Fig. 2 for layers 7 and 4 nm—others are not shown). To improve the performance of such a coating, it is necessary to optimize the thicknesses of the SiO_2 layers and get the maximum benefit from interference. The symmetric gradient coating has been modeled in TFCalc software, with the same material properties and effective thicknesses of metal island films as the deposited one [7]. The thicknesses of the dielectric layers were initially set to values of quarter-waves covering a range of 350–580 nm, changing gradually through the coating. The thicknesses of the SiO_2 layers have been free to optimize in order to achieve the maximal absorptance A of the design between 430 and 500 nm. Indeed, the optimization of the dielectric layer thicknesses improved the performance of the design. As shown in Fig. 6, the calculated absorptance peak after optimization is not asymmetric anymore. At the same time, the absorptance for the back-side light incidence is also improved, compared to the nonoptimized design. It must be highlighted once more that the bare substrate reflects some 4% of light in the visible part of the spectrum. For the sake of comparison with measured *Abs*, the spectra of the designs are also presented with the already included contribution of the back side of the substrate. In practice, to improve absorption and reduce reflection from this kind of device, the back side would be coated with a standard antireflective coating. In this way, *Abs* would increase and be comparable to *A*.

4. Conclusions

We have fabricated nongradient and gradient multilayer coatings, consisting of silver nanoparticle layers in a SiO_2 matrix. We show experimentally that multilayer systems with a gradient in the mass thickness of silver nanoparticles in the metal island film throughout the coating have higher absorption than equivalent nongradient coatings with the same total mass thickness of silver nanoparticles. The gradient systems show lower absorptance measured from the back side of the sample than the nongradient systems. The symmetric gradient system that we propose for the improvement of absorptance in this case combines the benefits from the condition for enhanced absorption with layers working as a gradient antireflective coating, improving the matching of impedances toward the ambient. After covering the bare side of the substrate with a common antireflective coating, it is possible to obtain comparable absorptances for both sides of light incidence.

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