Plasmon based antireflection coatings containing nanostructured Ag and silica medium

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ABSTRACT

The transmittance and scattering of the antireflection (AR) coatings based on nanostructured Ag and silica medium were enhanced by the exploitation of the localized surface plasmon resonance (LSPR). The transmittance and scattering values of AR coatings are relative to the annealing temperature, Ag concentration and thickness of AR coatings. The transmittance values of 95.7% and 97.2% of AR coatings with 0.10 wt.% Ag and annealed at 400 °C were obtained in the visible wavelength for a single-side and double-side coated glass slides, respectively. The enhanced transmittance and scattering of the AR coatings are primarily attributable to the large forward scattering of nanostructured Ag and the lesser refractive indices of Ag/SiO$_2$ coatings.

1. Introduction

Antireflection (AR) technology has been widely applied such as optical components, solar cells, flat panel displays and light emitting diode (LED) lighting, to increase the transmittance of incident light and prevent disturbances from external light [1–4]. The basic role of AR coating is destructive interference of the reflected light from air/coating and coating/substrate interfaces. For an ideal single layer AR coating on substrate, the refractive index (n_f) and thickness (d) of the AR coating should satisfy two criterions:

$$n_f = \sqrt{n_0 n_s} \tag{1}$$

and

$$d = \frac{\lambda_0}{4 n_f} \tag{2}$$

where n_f, n_0 and n_s are the refractive indices of the AR material, air and substrate, respectively [4,5]. Since the refractive indices of glass and transparent plastic substrates are ~1.52, the refractive index of the AR film on glass substrate should be 1.22 to meet zero reflectance at a specific wavelength. The strategy of introducing nanoporosity into the AR coating is an effective approach to obtain low refractive index of 1.22 [4–7].

The porous AR film with less than a few hundreds of nanometer thickness can efficiently avoid light scattering because the size of nanopores is much smaller than the visible light [8]. For applications to flat panel displays and optical components, this kind of AR coating not only increases the transmittance of light but also removes ghost images [4]. However, the AR coating with light scattering function would be better for applications to solar cells and LED lighting. The light scattering into solar cells from the AR coating can transfer more distance before reflection and is easily absorbed by the photoactive layer that reduces the thickness of the active layer and improves the power conversion efficiencies and decreases production costs of solar cells [9,10]. For LED lighting, after a spot LED light pass through the AR coating with scattering function, the light would be more mellow, comfortable and efficient for indoor illumination.

A feasible approach towards improving light scattering without increasing the thickness of the AR coating is the exploitation of the localized surface plasmon resonance (LSPR) [11,12]. The excitation of LSPR in metal nanoparticles can result in near-field concentration of light and scattering light, which are responsible for enhanced absorption of light and photocurrent of solar cells [12,13]. The scattering and absorption of metal nanoparticles depend on the size, shape, particle material and refractive index of the surrounding

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medium. The dependence of the transmittance of Ag nanoparticles based glass on the Ag size has been reported [14,15]. In this letter, we report the 95.7% transmittance of glass based on AR coating containing nanostructured Ag and silica medium by the LSPR.

2. Experimental details

The silica sol was prepared by a sol–gel method [4]. Ammonium hydroxide, deionized water, and ethanol were mixed in the reaction vessel. After the solution was heated to 50 °C, the tetraethyl orthosilicate (TEOS) dissolved in ethanol was quickly added to the vessel. TEOS:EtOH:H_2O:NH_4OH were mixed with a molar ratio of 1:38:0.9:1.6. The solution was stirred at a constant rate of 300 rpm for 12 h to get the silica sol. Here, we supposed TEOS to completely synthesize silica. The silver-nanowires with 80–100 nm diameter and 10–15 μm length were fabricated by typical polyol method [16,17]. The 1.0 mg silver-nanowires were added to 10 ml ethyl alcohol solution and the uniform Ag suspension was prepared by stirring for 6 h at room temperature. Then the Ag suspension was gradually dropped into the silica sol and continually stirred for 24 h to fabricate the Ag/SiO_2 colloids with nominal 0.025 wt.%, 0.05 wt.%, 0.10 wt.% and 0.20 wt.% Ag concentration, respectively. The Ag/SiO_2 colloids were spin-coated on top of the glass substrate to form ~120 nm thick Ag/SiO_2 coatings. The Ag/SiO_2 coatings were annealed with different temperature for 1 h under ambient atmospheric conditions. The morphology of the AR coating was examined by a field-emission scanning electrons microscope (FESEM S4800, Hitachi,) and an atomic-force microscope (AFM, NanoScope IIIa, Digital Instrument). The transmittance and reflectance of AR coating were measured by a UV–vis spectrophotometer (U-3900, Hitachi). The refractive index was measured using a Spectroscopic Ellipsometer (SC620).

3. Results and discussion

The light scattering by metallic nanoparticles consists of the forward scattering direction and backward scattering direction [12,18]. For the AR coating based on nanostructured Ag, the forward scattering can contribute to its transmittance, whereas the backward scattering can prohibit its transmittance. The sizes, shapes, nanostructured surface coverage, composition and the surrounding medium can influence the cross-sections for absorption, forward scattering and backward scattering that are tightly relative to the transmittance of the Ag/SiO_2 coatings. The large size of Ag nanostructures usually increases the cross-section area of scattering [12,14]. The transmittance of AR coating containing nanostructured Ag and silica medium with different annealing temperature was shown in Fig. 1(a). The silica sol doped with 0.10 wt.% Ag concentration was spin coated on top of the glass slide at the speed rate of 1000 rpm to form ~120 nm thick films. The maximum transmittance of AR coating was improved from 92% to 95.7% with increasing annealing temperature from 200 °C to 400 °C over 350–800 nm. The transmittance of AR coating with only silica film was gradually saturated in the range from 350 nm to 800 nm at annealing temperature over 300 °C, as shown in Fig. 1(b). This means that the morphology of silica film is no longer contributed to the enhanced transmittance at annealing temperature over 300 °C. The enhanced transmittance is expected to be primarily attributable to the shape variance of nanostructured Ag because Ag nanowires can be gradually increased the average diameter and shortened the average length of Ag nanowires between 200 °C and 300 °C due to the surface melting, which can happen at a temperature much lower than the melting point of bulk metal [19,20]. The shape variance of Ag nanowires over 200 °C has been demonstrated with SEM images in our research group [17]. This can be further
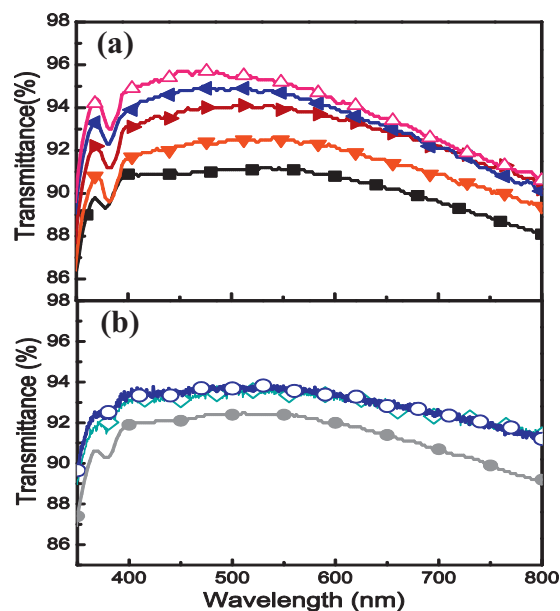

Fig. 1. Transmission spectra of Ag/SiO_2 AR coatings annealed at 200 °C (▼), 300 °C (►), 400 °C (△), 500 °C (◄) and pure glass slide (■) (a), pure SiO_2 coatings annealed at 300 °C (○), 400 °C (◇) and 80 °C (●) (b).

demonstrated that the maximum transmittance wavelength of AR coating annealed at 200 °C is red-shifted than that of AR coatings annealed at 300 °C, 400 °C and 500 °C, as shown in Fig. 1(a), because the longitudinal SPR wavelength is more sensitive to the shape than the transverse SPR and gradually shifted to the shorter wavelength when the aspect ratio of the Ag nanowires decreases [21]. However, the possibly reason that the decrease of the transmittance of AR coating annealed at 500 °C is that Ag nanowires have been completely converted into nanoparticles or specially shape which result in more increasing of their SPR absorption and decreasing of forward scattering comparing to AR coating annealed at 400 °C. Another possible reason is that the partial oxidization of Ag nanostructures at annealing temperature 500 °C would decrease the effective size of Ag nanostructures. We have demonstrated that the resistance of Ag films with several nanometers annealed at 500 °C due to the partial oxidization was obviously increased comparing to that of Ag films annealed at 400 °C.

Fig. 2 presents the transmittance of AR coatings with different Ag concentration. The nominal Ag concentration in silica medium
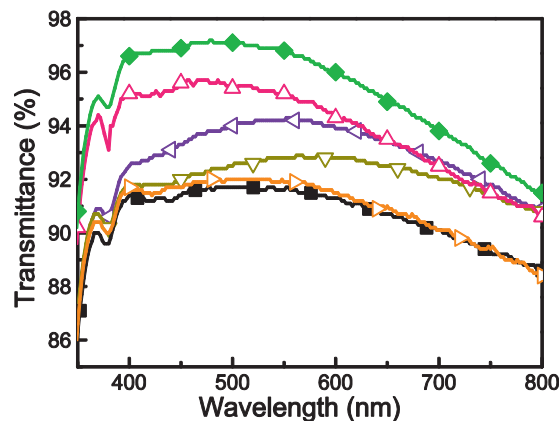

Fig. 2. Transmission spectra of AR coatings with Ag concentration of 0.10 wt.% (△), 0.05 wt.% (◁), 0.025 wt.% (▽), 0.20 wt.% (▷) for single-side coated glass slides, Ag concentration of 0.10 wt.% (◆) for the double-side coated glass slide, and uncoated glass slide (■).
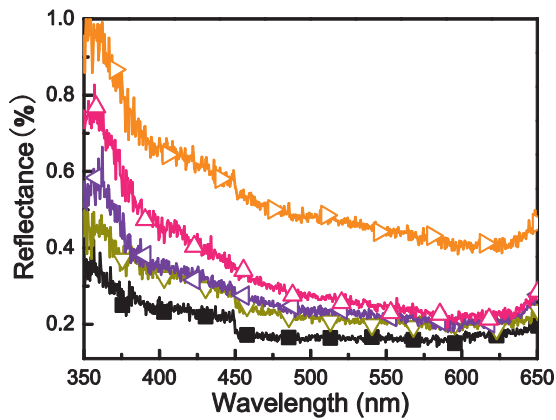
Fig. 3. Reflection spectra of glass slides with Ag/SiO$_2$ coatings with Ag concentration of 0.10 wt.% ($\triangle$), 0.05 wt.% ($\triangleleft$), 0.025 wt.% ($\triangledown$), 0.20 wt.% ($\triangleright$), and pure glass slide ($\blacksquare$).

is 0.025 wt.%, 0.05 wt.%, 0.10 wt.% and 0.20 wt.%, respectively. The AR coatings were spin coated on top of the glass slides, followed by annealing at 400 °C for 1 h under ambient atmospheric conditions. The transmittance at visible wavelength was gradually enhanced when Ag concentration was increased from 0.025 wt.% to 0.10 wt.%. The maximum transmittance of 0.10 wt.% Ag AR coating are 95.7% and 97.2% at the visible wavelength for single-side and double-side coated glass slides, respectively. The improving transmittance is possibly attributed to form the larger Ag nanostructures with increasing Ag concentration under annealing temperature 400 °C. The aggregation Ag nano-wires would melt into the larger size of Ag nanostructures at right annealing temperature. However, the transmittance of AR coating with 0.20 wt.% Ag concentration was decreased to 92% and close to that of pure glass slide. The results indicate that the transmittance of the glass with nanostructured Ag can be efficiently enhanced within the right range of the Ag concentration. The decrease transmittance of AR coating doped with 0.20 wt.% Ag concentration is attributable to the enhanced backward scattering of nanostructured Ag, as illustrated in Fig. 3. To clear the reflection of glass backside, the black ink was smeared on top of the glass backside. The reflection spectra were measured at normal incidence. Hence, the reflection of normal angle is out and the only reflection of oblique incidence can be collected by the integrating sphere. The enhanced backward scattering of AR coatings with increasing Ag concentration suggests that the transmittance of the AR coating was degraded.

As for AR coatings containing nanostructured Ag and silica, the interaction between silica medium and Ag nanostructures need to be investigated besides Ag nanostructures. The wavelength of maximum transmittance is blue-shifted when Ag concentration was increased from 0.025 wt.% to 0.10 wt.%, as illustrated in Fig. 2. This phenomenon apparently conflicts with the red-shifted wavelength of LSPR due to interactions between plasmons from individual Ag nanostructures as their separation is reduced with increasing Ag concentration [13]. To investigate the interaction between silica medium and Ag nanostructures, SEM and AFM images and refractive indices of AR coatings were measured, as shown in Fig. 4. The AR coatings were annealed at 400 °C for 1 h. The AR coatings with nanostructured Ag and silica medium have more abundant porosities than that of silica coating, as illustrated in Fig. 4(a) and (b). The refractive index of the Ag/SiO$_2$ coatings was only 1.12 at 550 nm, as shown in Fig. 4(c). The lesser refractive index of Ag/SiO$_2$ coating is attributed to the negative refractive index of Ag nanostructures and porous silica medium. For a single-layer coating, according to Eq. (2), λ_0 moves from a longer wavelength to a short wavelength with an decrease in n_f if the thickness of the coating is constant [4]. The lesser refractive index of Ag/SiO$_2$ coatings probably results in
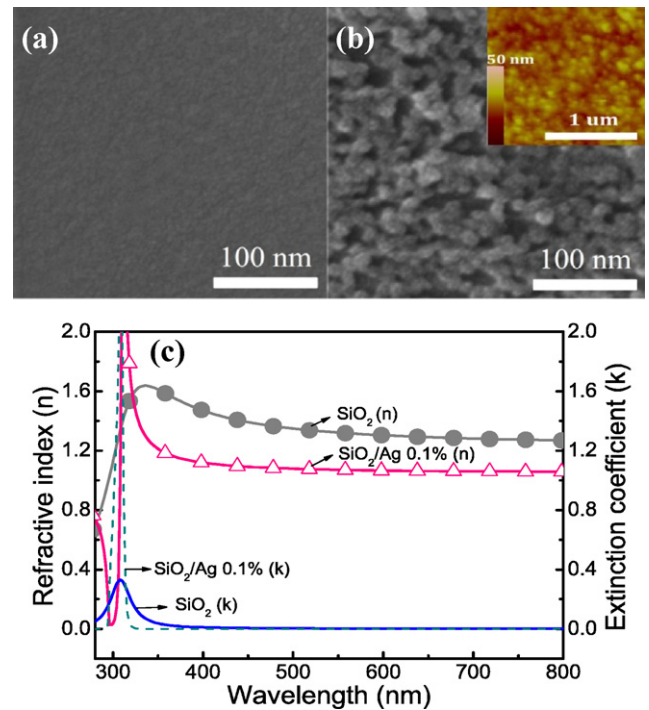

Fig. 4. SEM images of top morphology on glass slides coated with pure SiO$_2$ (a) and Ag/SiO$_2$ film with Ag concentration of 0.1 wt.% (b) (inset of figure (b): AFM image of Ag/SiO$_2$ coating). (c) Refractive index and extinction coefficient of pure silica film and Ag/SiO$_2$ film with Ag concentration of 0.1 wt.%.

the blue-shifted transmittance spectra of Ag/SiO$_2$ coatings when Ag concentration increased from 0.025 wt.% to 0.10 wt.%. However, the wavelength of maximum transmittance of Ag/SiO$_2$ coatings with doped with 0.10 wt.% Ag nanowires is blue-shifted with increasing thickness of AR coatings from 52 nm to 120 nm, as illustrated in Fig. 5, which is inconsistent with the preconception of Eq. (2). It cannot also explain from Eq. (2) that the transmittance of Ag/SiO$_2$ coating doped with 0.20 wt.% Ag nanowires was fleetly decreased comparing to Ag/SiO$_2$ coating with 0.10 wt.% Ag. The increasing nanostructured Ag surface coverage and interaction between plasmons from individual Ag nanostructure seem to explain these phenomena because the variance of its surface coverage and interaction between Ag nanostructures can influence the cross-section areas for absorption, forward and backward scattering. Its direct and clear evidence still need to be further studied in the future. However, our experimental results may roughly suggest that LSPR
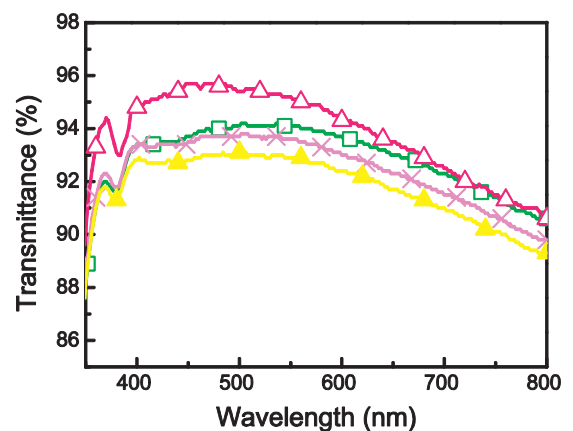

Fig. 5. Transmission spectra of glass slides with Ag/SiO$_2$ coatings with the thicknesses of 135 nm ($\square$), 120 nm ($\triangle$), 87 nm ($\times$), 52 nm ($\blacktriangle$).

of nanostructured Ag and the lesser refractive indices of Ag/SiO$_2$ coating are together responsible for enhanced transmittance.

4. Conclusions

In summary, we developed a method of fabricating the AR coating based on nanostructured Ag and the silica medium. The maximum transmittance of 95.7% and 97.2% at visible wavelength were achieved for single-side and double-side coated glass slides, respectively. The transmittance and scattering of the AR coating is enhanced by the LSPR of nanostructured Ag. The lesser refractive indices of Ag/SiO$_2$ coatings are also helpful to improve the transmittance of the AR coating. The AR coating with nanostructured Ag and silica medium is expected to further improve the absorption of solar cells and helpfully fog the LED spot light due to its light scattering.

Acknowledgements

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