Tunable surface-plasmon-resonance wavelength of silver island films*

Wang Ji-Fei(王继飞)[a], Li Hong-Jian(李宏建)[a)b)†], Zhou Zi-You(周子游)[a], Li Xue-Yong(李雪勇)[b], Liu Ju(刘 菊)[a], and Yang Hai-Yan(杨海艳)[a]

[a] *College of Physics Science and Technology, Central South University, Changsha* 410083, *China*
[b] *School of Materials Science and Engineering, Central South University, Changsha* 410083, *China*

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This paper experimentally and theoretically investigates the effect of the underlayer medium on tuning of the surface plasmon resonance (SPR) wavelength of silver island films, and the effect of substrate temperature on the morphologies and optical properties of the films. From the absorption spectra of single Ag with various thickness and overcoated (Ag/TiO_2) films deposited on glass substrates at various substrate temperatures by RF magnetron sputtering, we demonstrate that the surface plasmon resonance wavelength can be made tunable by changing the underlayer medium, the thickness of metal layer and the substrate temperature. By varying substrate temperatures, the interparticle coupling effects on plasmon resonances of nanosilver particles enhance as the spacing between the particles reduces. When the substrate temperature is up to 500 °C, the absorption peak decreases sharply and shifts to shorter wavelength side due to the severe coalescence between silver islands in the film.

Keywords: Ag/TiO_2 island thin film, surface plasmons, absorption spectrum, substrate temperature
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1. Introduction

Metallic island films have the potential to significantly increase the energy conversion efficiency of solar cell, due to their particular optical characterisation. The films are usually formed by noble metal nanoparticles, such as Ag, Au, and Cu, due to their free electron like behaviour and can support surface plasmon modes. The islands are nanometer sized and with low nobel metal mass thickness (< 10 nm). When the frequency of the incoming light is in resonance with these modes, it will result in induced charged density oscillation and show a strong absorption maximum at a particular wavelength, called the surface plasmon resonance (SPR) wavelength, which is a major mechanism for surface-enhanced Raman spectroscopy (SERS).[1]

Many applications of these metal nanoparticles thin films have been proposed, taking advantage of the optical response at the SPR. Recent studies[2,3] exploiting metal nanoparticles on top of inorganic Si diodes have displayed increased absorption and increased photocurrent response. Previously, organic small molecules have been coevaporated together with metal clusters to excite localised plasmons that couple to the active material, demonstrating both increased absorption and photocurrent.[4,5] Rand *et al.*[6] had investigated the effect of the optical properties of silver nanoparticles used in tandem ultrathin-film organic photovoltaic cell, which indicated that the enhancement of an incident optical field persists into an organic dielectric for distances of up to 10 nm from the centre of an array of approximately 5-nm-diameter nanoparticles. Furthermore, the applications of these metal nanoparticles thin films including in surface-enhanced Raman scattering,[7] optical tweezers, labels for bimolecules, surface enhanced second harmonic generation,[8] and for the development of colour filters,[9,10] sensors, and all-optical switching devices.[11] In the interest of enhancing the efficiency of the solar cells, to make full use of the solar light is a simplest and most effective way. An efficient technique is to use the noble metals such as Ag, Au and Cu nanoparticles thin films to enhance the absorption of solar light due to their particular optical characterisation, that is, the SPR. What of great significance is the

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†Corresponding author. E-mail: lihj398@yahoo.com.cn
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ability to tune and extend the SPR wavelength, which is highly desirable in various applications of metallic nanoparticles.

In this paper, we first investigate the effect of the thickness of Ag island film and the surrounding medium on the tuning and extending of the SPR wavelength of silver island film. In order to vary inter-island dielectric constant, $\varepsilon_{\rm av}$, we introduce the dielectric medium TiO_2 to coat the substrate before silver island films deposition. We also discuss the effect of the substrate temperature on morphologies and optical characterisation of Ag island films coating with TiO_2 medium experimentally and theoretically. It shows that the variations of the thicknesses of Ag and TiO_2 medium can tune the SPR wavelength in a large range, and also the structure of the TiO_2 thin films can affect the absorption efficiency and the tunability of SPR wavelength of silver island thin films effectively.

2. Experimental

2.1. Preparation of Ag island thin films and Ag/TiO_2 thin films

The Ag island films are deposited by RF magnetron sputtering, which consists of a cylindrical chamber connected to a turbo molecular pump. Ag island films are fabricated on plain microscope glass slide so that the interaction between the substrate and nanoparticles is minimised, using 99.99% pure Ag metallic target by dc magnetron sputtering. The base pressure in the chamber is 5×10^{-4} Pa and the distance between the target and substrate is set at 70 mm. The glass substrates are first cleaned in propanone and ethyl alcohol solution in an ultrasonic bath for 10–15 min, rinsed in deionised water and finally dried in high purity N_2 gas stream. The deposition time is kept shorter than the time required to form a continuous layer. In order to investigate the effect of the substrate, we deposit the dielectric medium TiO_2 (99.9% purity) in Ar at continuous substrate temperature (room temperature–500 °C), which have different SPR wavelength and absorbance efficiency, on glass substrate prior to silver deposition. During deposition, the substrate is rotated with a frequency of 30 r/min, while the power, deposition pressure, (flow rate of argon) are kept constant as 10 W, 1 Pa (40 sccm) for Ag, and 80 W, 0.5 Pa for TiO_2. Before each run, targets are pre-sputtered in a pure argon atmosphere for 10 minutes to clean the surface of the targets.

2.2. Characterisation

Optical absorption of the assembly is measured at room temperature with a UV–VIS spectrophotometer (TU-1800PC) over the wavelength range from 300 to 1100 nm referenced to clean plain microscope glass slide to cancel out absorption losses of the substrate. Morphology observation of the thin films is carried out on an atomic force microscope (AFM, Solver P47).

3. Results and discussion

3.1. Experiment results

3.1.1. Characterisation of Ag island thin films

Metal nanoparticles have fixed surface plasmon polariton resonant wavelength. Incident light, in the region of the resonant wavelength, is strongly absorbed or scatteredd. We have prepared five nano-Ag island thin films first, which are deposited with different thicknesses at room temperature. We here depict the results with the silver mass thickness rather than the particle filling factor of metallic islands q (i.e., volume fraction of the metal component in the island film) since the silver mass thickness can be directly obtained in the experiments. As a rule of thumb, the mass thickness is monotonically varying with q. Figure 1 shows the absorption spectra of Ag islands with different thickness.

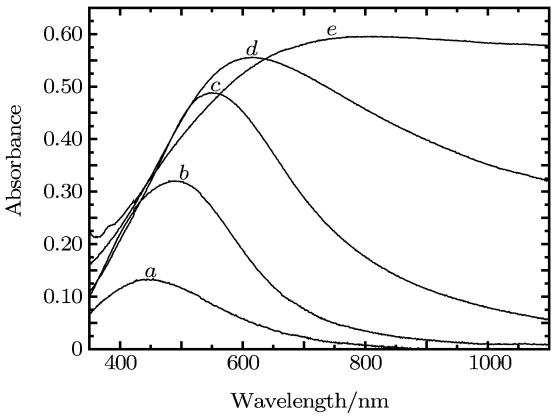


Fig. 1. Absorption spectra of silver islands on bare glass substrate with various mass thicknesses of Ag island thin films: curve a 1.8 nm, curve b 2.7 nm, curve c 3.6 nm, curve d 5.4 nm, and curve e 7.2 nm, the substrate is at room temperature (RT).

The curves exhibit the characteristic absorption of metal island films; the plasmon resonant peaks shift to longer wavelength side and broaden with increasing thickness of the Ag island film, accompanied by an ever-increasing intensity. Nevertheless, the films deposited with a thcikness of 5.4 nm (curve *d*) have the redshifted enhancement tail that extends well beyond the absorption of most organic PV materials, making this structure of the film better suited for use in organic PV cells. Three reasons are thought to be responsible for the change of the spectra. One is the particle shape and size distribution. The position and intensity of the peaks are indicative of a distribution in particle shape and size.[7] With increasing thickness of Ag thin films, nanoparticles with larger in-plan (X–Y) dimensions are formed, causing the effect of scattering greater than absorption. So the absorption peaks redshift. In addition, the SPR bands become broader when the size and shape distributions of Ag nanoparticles become more irregular. The second reason is the increase in the dipolar coupling between particles with decreasing particle spacing, which would likely provide an additional absorption on the long wavelength side of the spectrum[12] and broaden the optical response.[13] The last one is the larger enhancement of free-electron damping in the dielectric constant of silver as the wavelength increases.[14] We can also note that the thickness of Ag films cannot exceed a certain value, for the separated islands will contact with each other and form an aggregate structure of the film. In this case, the SPR of Ag nanoparticles decreases or even vanishes.

3.1.2. Characterisation of Ag/TiO_2 island thin films

The ability to tune and extend the SPR wavelength is highly desirable in various applications of metallic nanoparticles. The SPR depends on the particle size, shape, filling factor (i.e., volume fraction of the metal component in the island film), and the dielectric properties of the metallic island itself, which have been discussed above. In addition, the surrounding dielectric medium is a critical parameter.[15–17] The inter-island dielectric constant, $\varepsilon_{\rm av}$, of the metallic islands is usually an average of the dielectric constants of the substrate, $\varepsilon_{\rm sub}$, and the external surrounding medium, $\varepsilon_{\rm ext}$, i.e., $\varepsilon_{\rm av} = n^2 = (\varepsilon_{\rm sub} + \varepsilon_{\rm ext})/2$.[18] Changing the substrate material may obtain some tunability in SPR.[19] We here introduce the medium TiO_2 to interpret the effect of the underlayer medium on the tuning and extending of the SPR wavelength. Figure 2 shows the absorption spectra of Ag islands films with and without a coating medium (TiO_2). The thickness of Ag island is 2.7 nm.

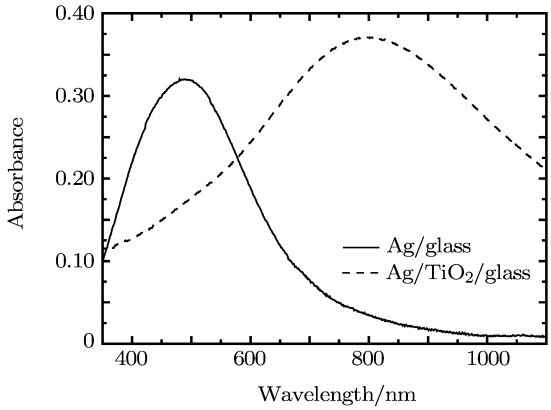


Fig. 2. Absorption spectra of silver islands on a bare glass without any coating and coating with TiO_2, the thickness of Ag island is 2.7 nm and that of TiO_2 is about 10 nm.

The SPR wavelength $\lambda_{\rm spr}$ corresponds to that at an absorption tip in each curve. From Fig. 2, one can see that the effect of the TiO_2 layer on absorption spectra is remarkable; $\lambda_{\rm spr}$ can be readily shifted across the visible region. In detail, for Ag islands on bare glass, i.e., the typical case of Ag island film substrate, the SPR wavelength centres about 450 nm and can be adjusted in a narrow range in the visible region, namely $440 \leq \lambda_{\rm spr} \leq 564$ nm . As a consequence, the tunability for the films coating with TiO_2 is enhanced, and $\lambda_{\rm spr}$ shifts from 468 to 798 nm accompanied by an increase in intensity, resulting in a 16.6% absorption efficiency higher than the typical Ag island film substrate. Also, notice that the resonance band becomes broader as the substrate with a higher refractive index is used. The silver on the underlayer of TiO_2 ($n = 2.75$) is compared with that on bare glass ($n = 10$). compared. The former shows much broader peaks with $\lambda_{\rm spr}$ extending to the infrared, while the latter shows narrow absorption peaks with $\lambda_{\rm spr}$ in the blue region. This is a common feature accompanying the redshifts of $\lambda_{\rm spr}$ for metallic island films formed through a natural growth process.[20] Two reasons are thought to be responsible for this broadening. One is the particle shape dispersion.[16] The other is the increasingly enhanced free-electron damping in the dielectric constant of silver when the wavelength increases.[14] In fact, the SPR band can be decomposed into a series of small absorption peaks

determined by the shape distributions. At short wavelengths all the small peaks show narrow width due to the low free-electron damping, whereas at longer wavelengths they become wider since the damping increases. Consequently, their summation, viz., the SPR band, exhibits the same dependence on wavelength; the larger the λ_{spr}, the wider the band.

3.1.3. The effect of substrate temperature on the tuning and extending of the SPR wavelength

The mechanisms of particle growth are strongly dependent on the surface migration of adatoms and nanoparticles, which is affected by substrate temperature (T_s).[21] We have prepared the Ag/TiO_2 island films at different substrate temperatures, and then studied the effects of substrate temperature on their morphology and optical characterisation.

Figure 3 shows the absorption spectra of Ag island films with a coating medium (TiO_2) at the substrate temperature ranging from RT to 500 °C. The thickness of Ag islands is 2.7 nm.

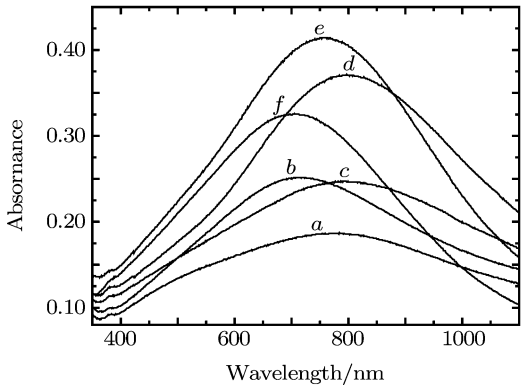


Fig. 3. Absorption spectra of silver islands coating with TiO_2 at substrate temperature: curve *a* room temperature, curve *b* 100 °C, curve *c* 200 °C, curve *d* 300 °C, curve *e* 400 °C and curve *f* 500 °C.

From Fig. 3, one can find that the substrate temperature is a critical parameter affecting the SPR wavelength. The SPR wavelength λ_{spr} shifts to longer wavelength when the substrate temperature increases from 100 °C to 300 °C. As the temperature is beyond 300 °C, λ_{spr} shifts backward to shorter wavelength. Furthermore, the absorption efficiency decreases sharply as the temperature is up to 500 °C and λ_{spr} blueshifts all the same. Thus, two mechanisms are considered to interpret the phenomenon. One is the formation of higher refractive index TiO_2 films with increasing substrate temperature and the interparticle coupling effects on plasmon resonance of nanosilver plasmon. It is well-known that the substrate temperature is a critical parameter affecting the structure of the TiO_2 film. Amorphous, anatase and Rutile TiO_2 thin films can be deposited at temperatures 100–150 °C,[22] 300–365 °C, and above 700 °C respectively. At the transition, the optical properties of TiO_2, such as refractive index, extinction coefficient changed. Hovel[23] has published two excellent graphs demonstrating the trend of increasing refractive index with increasing deposition temperature. It leads to the increase in dielectric function, then the SPR wavelength λ_{spr} shifts to longer wavelength. It is not necessary to study the effect of the rutile film for the SPR wavelength λ_{spr} decrease at 500 °C. In addition, increasing the substrate temperature at low temperatures (below 300 °C) would produce films with smaller size and higher density. In this case, the spacing between the particles reduces, interparticle coupling effects on plasmon resonance of nanosilver plasmon are stronger than the shape effect.[24] Thus the plasmon resonant peaks significantly shift to higher wavelength. The other mechanism considered is the coalescence effects in the Ag island films. We will discuss it with the AFM images of the thin films later.

3.1.4. AFM analysis

Figure 4 shows the AFM images of the Ag island films coated with TiO_2 medium, the substrates temperatures are RT, 100 °C, 200 °C, 300 °C, 400 °C and 500 °C respectively, The thickness of Ag islands is 2.7 nm.

At low temperatures, below 300 °C , the principal effects of substrate temperature are annealing the growing metal island, reducing the island size, and increasing the nanoparticle density (Figs. 4(b), 4(c), and 4(d)), because the high migration rate reduces the coalescence growth. Therefore, increasing the substrate temperature at low temperatures would produce films with smaller size and higher density. At higher temperatures (above 300 °C), significantly more surface diffusion of adatoms occurs on the substrate, and small nanoparticles are able to migrate and relax to form nanoparticles with larger in-plan (X–Y) dimensions (Figs. 4(e) and 4(f)). The Ag nanoparticles begin to touch each other and islands began to coalesce when the substrate temperature is beyond 400 °C, the λ_{spr} shifts to shorter wavelength accompanied by the decrease in absorption efficiency. Thus, the experimental results we observe in Fig. 4 might be

considered as the competition of the two mechanisms that lead to the tunability of the SPR wavelength. Furthermore, we also find that the resonance band of the film deposited at RT is broader and the SPR wavelength λ_{spr} is longer than that of the films deposited at 100 °C and 200 °C. Indeed, the clusters grown at cold substrates typically present a wider size and shape distribution and higher percolation degree,[25] resulting in an increase in the cluster–cluster interaction and leading to a broader SPR wavelength.[26,27] With the particle shapes changing from oblate spheroid to sphere, the SPR wavelength λ_{spr} decreases. We will explain the phenomenon with Maxwell–Garnett Theory later.

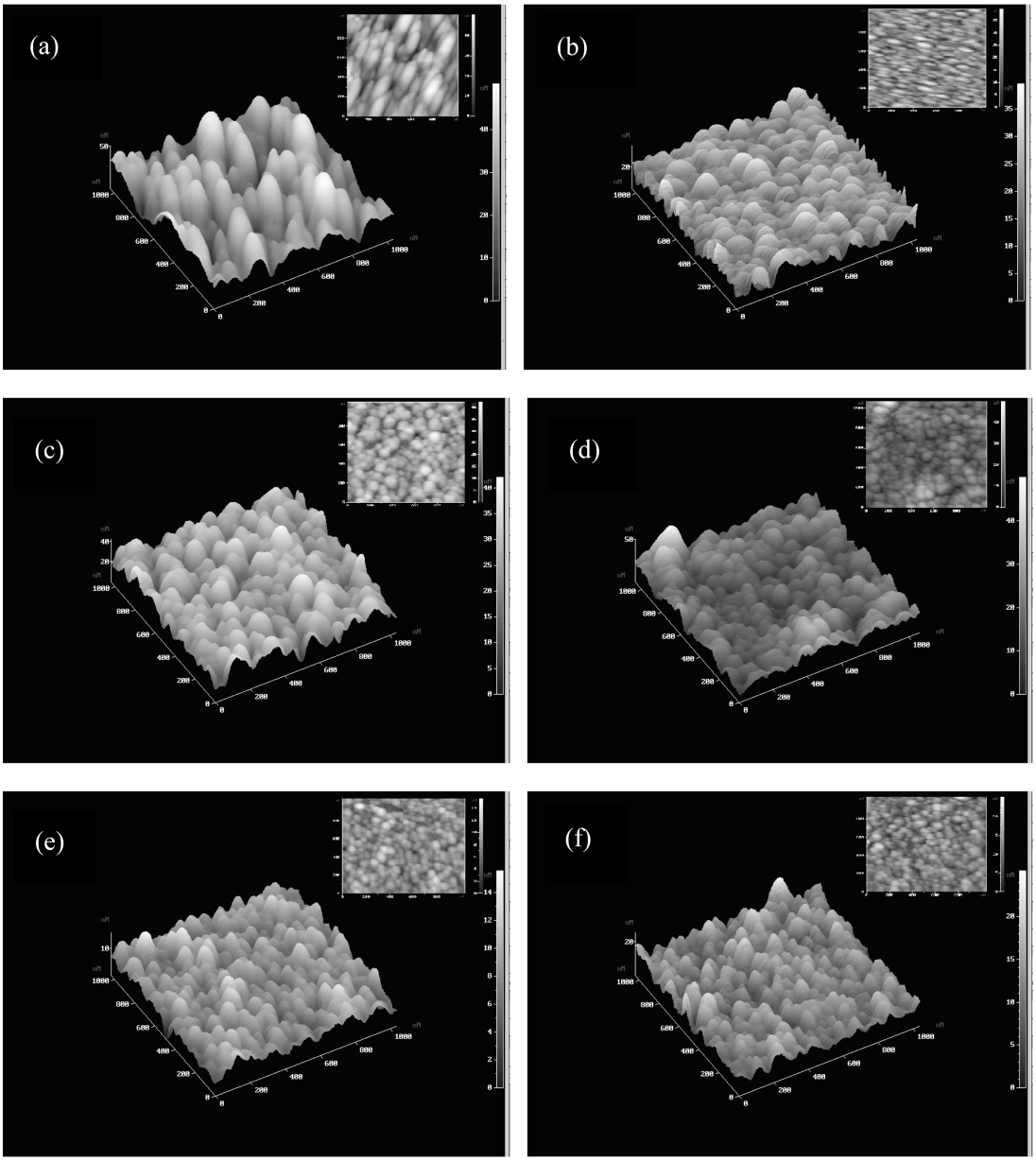


Fig. 4. AFM images of the Ag island films coated with TiO_2 prepared at various substrate temperatures. (a) RT, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C. The thickness of Ag islands is 2.7 nm.

3.2. Theoretical framework of the optical simulation

3.2.1. Maxwell–Garnett theory

The optical properties of a metallic island film can be regarded as those of a composite material system, consisting of mixtures of metallic grains and insulators (air or the substrate material). Maxwell–Garnett (MG) theory is one of the well-know approximations,

which is applicable to the separated-grain structure in which particles of one component are embedded in a continuous medium of the other component. As to the silver island film, the metallic islands obviously correspond to the particle component and the substrate and/or air correspond(s) to the medium component. The effective dielectric constant of the island film in this case is expressed as

$$\frac{\xi^{\mathrm{MG}}-\varepsilon_{\mathrm{av}}}{L\xi^{\mathrm{MG}}+(1-L)\varepsilon_{\mathrm{av}}}=q\frac{\varepsilon_{\mathrm{m}}-\varepsilon_{\mathrm{av}}}{L\varepsilon_{\mathrm{m}}+(1-L)\varepsilon_{\mathrm{av}}}, \quad (1)$$

where $\varepsilon_{\mathrm{av}}$ is the inter-island dielectric constant defined previously ($\varepsilon_{\mathrm{av}}$ is real here), $\varepsilon_{\mathrm{m}}(=\varepsilon_{\mathrm{m1}}+\mathrm{i}\,\varepsilon_{\mathrm{m2}})$ is the dielectric constants of the metallic particles, q is particle filling factor of metallic islands. L is the depolarisation factor that accounts for the mean shape of the inclusions.

For oblate particles L is given by[28]

$$L=\frac{1-e^2}{2e^3}\left(\ln\frac{1+e}{1-e}-2e\right), \quad (2)$$

where e is the eccentricity defined as $e=(1-\gamma^2)^{1/2}$ with $\gamma=b/a$, the axial ratio, where a, b are the half-axes of the spheroid. For a real metal, its dielectric constant ε_{m} can be described with a Drude model, namely

$$\varepsilon_{\mathrm{m1}}=\varepsilon_{\infty}-\frac{\omega_{\mathrm{p}}^2}{\omega(\omega^2+\omega_0^2)}, \quad (3)$$

$$\varepsilon_{\mathrm{m1}}=\frac{\omega_{\mathrm{p}}^2\omega_0}{\omega(\omega^2+\omega_0^2)}, \quad (4)$$

where ω_{p} and ω_0 are respectively the free-electron plasma frequency and collision frequency. Notice that the bound electron contributions to ε_{m} is included in ε_{∞}. The SPR frequency is defined as the frequency for which $\mathrm{Re}[\xi(\omega_{\mathrm{spr}})]=0$.[29] Substituting Eqs. (4) and (5) into Eq. (1) and solving it under this condition, we obtain

$$\omega_{\mathrm{spr}}^2=\omega_{\mathrm{p}}^2\frac{(1-q)L}{\varepsilon_{\mathrm{av}}-(\varepsilon_{\mathrm{av}}-\varepsilon_{\infty})(1-q)L}-\omega_0^2. \quad (5)$$

It was demonstrated that ω_0 has very limited effects on ω_{spr} and can be dropped in Eq. (5). Thus, the SPR wavelength $\lambda_{\mathrm{spr}}(\equiv 2\pi c/\omega_{\mathrm{spr}})$ is given by

$$\lambda_{\mathrm{spr}}=\lambda_{\mathrm{p}}\left[\frac{\varepsilon_{\mathrm{av}}}{(1-q)L}-\varepsilon_{\mathrm{av}}+\varepsilon_{\infty}\right]^{1/2}, \quad (6)$$

where $\lambda_{\mathrm{p}}=2\pi c/\omega_{\mathrm{p}}$ is the metal's bulk plasma wavelength. For the spherical particle ($L_{\mathrm{m}}=1/3$) in air ($\varepsilon_{\mathrm{av}}=1$) and exclude bound-electron contribution ($\varepsilon_{\infty}=1$). When $q\to 0$, this equation is further reduced to the result obtained by Mie's theory.[30] From Eq. (6), it is certain that addition of TiO_2 to the particles causes λ_{spr} to redshift, as in Fig. 2, since the dielectric constant, ε, of the surrounding medium ($\varepsilon_{\mathrm{TiO_2}}=5.76$) increases as compared to air ($\varepsilon_{\mathrm{air}}=1$). Also from Eq. (2), we notice that the increase of the axial ratio, γ, yields a decrease in λ_{spr}. That is, λ_{spr} shifts to shorter wavelength if the particles change their shapes from oblate spheroid to sphere, as shows in Figs. 3(a) and 3(b). From the AFM image (Fig. 4(a)), one can find that their shapes are oblate spheroid with smaller axial ratio. With these particle shapes changing from oblate spheroid to sphere (Fig. 4(b)), the SPR wavelength λ_{spr} decreases.

Equation (6) is invalidated in the metal-rich limit ($q\to 1$) because the neighbouring metal particles contact each other and form an aggregate structure. In this case, it is reasonable to consider the film to consist of dielectric inclusions in a continuous metal matrix, rather than metal particles in a continuous dielectric matrix, which is given by[31]

$$\lambda_{\mathrm{spr}}=\lambda_{\mathrm{p}}\left[\frac{qL_1}{1-qL_1}\varepsilon_{\mathrm{av}}+\varepsilon_{\infty}\right]^{1/2} \quad (7)$$

with L_1 being the depolarisation factor of dielectric inclusions as $L_1\to 1$.

3.2.2. Optical simulation

Figure 5(a) shows a general result of λ_{spr} varying with filling factor $\varepsilon_{\mathrm{av}}$ in the case of different q. One can find that the SPR wavelength λ_{spr} generally shifts to longer wavelength with increasing $\varepsilon_{\mathrm{av}}$, which is consistent with the experimental results (Fig. 2). In the case of a large $\varepsilon_{\mathrm{av}}$, the curve displaces to higher level of λ_{spr} and at the same time becomes steeper. Figure 5(b) shows the dependence of λ_{spr} on q and $\varepsilon_{\mathrm{av}}$ from another view in contrast to Fig. 5(a). The SPR wavelength λ_{spr} generally shifts to longer wavelength with increasing q, showing the so-called size effect that is obviously enhanced if a larger $\varepsilon_{\mathrm{av}}$ is applied. It is clear that the inter-island dielectric constant $\varepsilon_{\mathrm{av}}$ can greatly extend the tunable wavelength range, in particular in the case of the film with a high q values. The dashed curves in Figs. 5(a) and 5(b) are obtained from the Eq. (7). It shows that, if the separated particles begin to aggregate or coalesce, an apparent blueshift in λ_{spr} should occur (the solid curve transforms to the dashed curve). It is in agreement with the experimental results, in which the SPR wavelength λ_{spr} blueshifts, when the thickness of Ag islands exceeds a certain value, and leads to the coalescence between islands in the thick film.

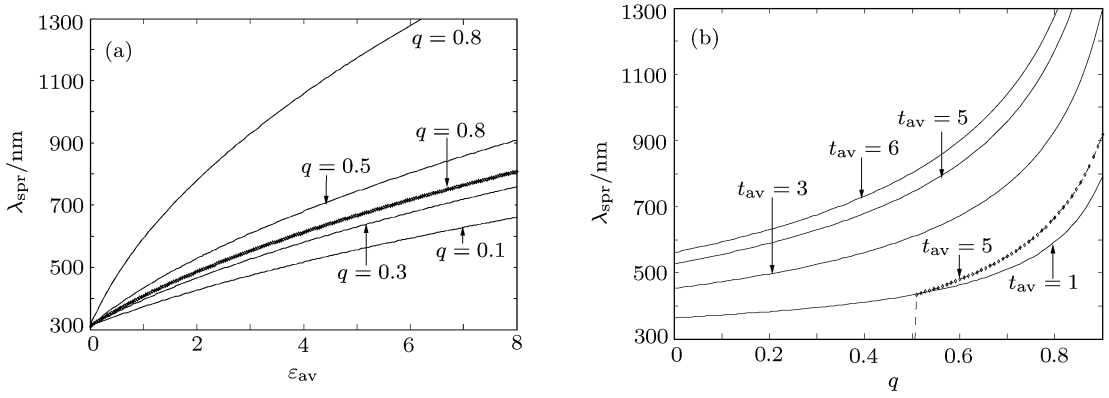


Fig. 5. The dependence of the SPR wavelength on (a) the inter-island dielectric constant ε_{av} in the case of different filling factors q, and (b) the filling factor q of metallic islands with different inter-island dielectric constant ε_{av}. Parameters used: $L_m = 1/3$, $L_1 = 0.99$, $\omega_p = 9.2$ eV, and $\varepsilon_\infty = 5.266$.

4. Conclusion

In summary, we have investigated the effect of the thickness of Ag islands, the underlayer medium and the substrate temperature on th tuning and extending of the SPR wavelength of sputtered silver island thin films. The capability of tuning the resonant wavelength can be effectively enhanced by increasing the refractive index of the substrate and the thickness of the metallic islands. The SPR wavelength of a standard silver island film can be readily adjusted from around 432 nm to 798 nm in the near infrared region. In addition, the substrate temperature is also a critical parameter. With increasing substrate temperature, interparticle coupling effects on plasmon resonances of nanosilver particles enhances with the decrease of the spacing between the particles. Furthermore, the TiO_2 films range from amorphous to anatase phase, causing the optical parameters change and the refractive increases. In this case, the SPR wavelength λ_{spr} can be readily adjusted from around 698 nm to 810 nm. As the substrate temperature is beyond 400 °C, the Ag islands begin to coalesce and the SPR wavelength λ_{spr} shifts to shorter wavelength.

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