JOURNAL OF APPLIED PHYSICS **104**, 053102 (2008)

Nano-Ag on vanadium dioxide. II. Thermal tuning of surface plasmon resonance

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(Received 13 May 2008; accepted 24 July 2008; published online 2 September 2008)

Thermal tuning of the localized surface plasmon resonance (LSPR) of Ag nanoparticles on a thermochromic thin film of VO_2 was studied experimentally. The tuning is strongly temperature dependent and thermally reversible. The LSPR wavelength λ_{SPR} shifts to the blue with increasing temperature from 30 to 80 °C, and shifts back to the red as temperature decreases. A smart tuning is achievable on condition that the temperature is controlled in a stepwise manner. The tunable wavelength range depends on the particle size or the mass thickness of the metal nanoparticle film. Further, the tunability was found to be enhanced significantly when a layer of TiO_2 was introduced to overcoat the Ag nanoparticles, yielding a marked sensitivity factor $\Delta\lambda_{SPR}/\Delta n$, of as large as 480 nm per refractive index unit (n) at the semiconductor phase of VO_2. *© 2008 American Institute of Physics*. [DOI: 10.1063/1.2973341]

I. INTRODUCTION

Noble metal nanoparticles have attracted a considerable interest for their unique optical properties characterized by localized surface plasmon resonance (LSPR). Generally, LSPR is excited when the incident light with a specific wavelength interacts with the metal nanoparticles to create the collective oscillation of conduction electrons. This LSPR is accompanied by wavelength-selective photon absorption and resonant Mie scattering and by a dramatic enhancement of the local electromagnetic field in the vicinity of the nanoparticles.[1–3] Such unique optical properties make the metal nanoparticle extremely valuable in a variety of technological applications such as plasmon-based optical devices,[4] chemical and biological sensors,[5,6] and surface-enhanced spectroscopies.[7,8]

Most of the above mentioned applications require the LSPR wavelength (λ_{SPR}) tunable over a wide spectral range. In view of the fact that λ_{SPR} depends on the size, shape, and composition of the metal nanoparticles, as well as on the surrounding dielectric environment,[2–4] the tunable wavelength range from visible to near infrared (NIR) regions has been achieved by varying these parameters.[3,9–12] However, almost all of those tuning methods are independent of temperature since the resonance of noble metal nanoparticle is known to be an electronic mechanism and insensitive to temperature.[13–16] It has been demonstrated that there was little change in the λ_{SPR} of Ag nanoparticle when the particles were heated from room temperature up to 500 °C.[13] Such a behavior of the noble metal nanoparticles may hinder their applications in temperature-sensitive optical devices or sensors.[6,17]

On the other hand, VO_2 is a well-known thermochromic material. It undergoes a reversible first-order semiconductor-metal transition (SMT) at critical temperature $t_c \approx 68$ °C, resulting in dramatic change in electrical and optical properties.[18–20] Of particular interest is the optical change through the SMT in the IR region where VO_2 varies from being transparent in the semiconductor phase to highly reflective in the metal phase, implying that the refractive index of VO_2 changes with temperature.[20] Hence, thermal tuning of the resonance of the metal nanoparticles can be achieved by taking advantage of this optical change in VO_2 stimulated by temperature.

Recently, such a thermal tuning of the resonance has been demonstrated.[21–25] Xu *et al.*[21] reported the temperature tunability of λ_{SPR} of Ag nanoparticle on VO_2 substrate. Also, a similar study was carried out by Maaza *et al.*[23,24] with Au nanoparticles dispersed in the VO_2 matrix.

Following our previous study mentioned above, in this work we investigate in detail how the λ_{SPR} of Ag nanoparticle is affected by SMT of VO_2. It demonstrates that λ_{SPR} is strongly temperature dependent and reversibly tunable. A smart tuning of λ_{SPR} can be achieved by controlling the external temperature in a stepwise manner. The tuning wavelength range is highly correlated with the particle size or the mass thickness of the nano-Ag film. A high-index dielectric medium TiO_2 was introduced to overcoat the Ag nanoparticles for both wavelength tuning and protecting Ag surface from photochemical degradation by absorbed species. Strikingly, it reveals that upon addition of TiO_2 the wavelength tunability of nano-Ag on VO_2 is enhanced significantly.

II. EXPERIMENTS

The fabrication methods for the two series of composite films of nano-Ag/VO_2 and TiO_2/nano-Ag/VO_2 with various Ag mass thicknesses were described in the prior Paper.[26] The thickness of the VO_2 layer is ~50 nm. For comparison, a Ag nanoparticle film with mass thickness of 10 nm was also deposited onto a bare sapphire slide, which is referred to as

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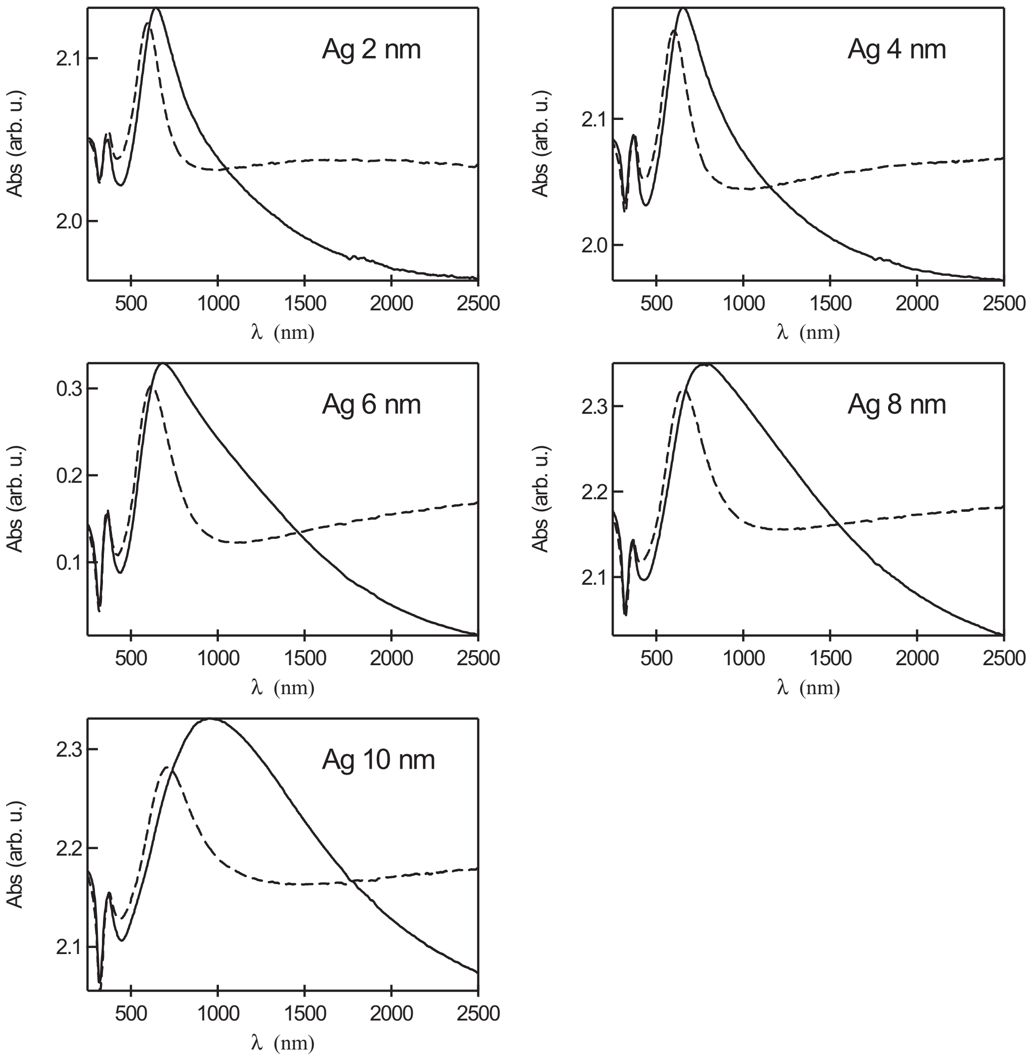

FIG. 1. Absorbance spectra of the AVS samples with various Ag mass thicknesses for both of the semiconductor (solid curves) and the metal (dashed curves) phases.

AS. The samples with a layer configuration of nano-Ag/quartz, nano-Ag/VO_2/sapphire, and TiO_2/nano-Ag/VO_2/sapphire are named as AQ, AVS, and TAVS, respectively.

Atomic force microscopy images of these samples were collected on a Nanoscope III scanning probe microscope (Digital Instruments) operated in tapping mode and the results were presented in the prior Paper.[26] Absorbance spectra of these samples were recorded on a UV-vis-NIR spectrophotometer (V-570, Jasco) with an attachment to control the external temperature of the samples. A silver-free VO_2-coated sapphire substrate was used as the reference during the measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows the absorbance spectra of AVS samples with various Ag mass thicknesses (d_m=2, 4, 6, 8, and 10 nm). The solid curves in this figure correspond to the semiconductor phase of VO_2 measured at 30 °C and the dashed curves correspond to the metal phase at 80 °C. It can be seen in the figure that the λ_{SPR} of Ag nanoparticles shifts to the blue when temperature increases from 30 to 80 °C for all of the five samples. It is well established that the SPR of noble metallic particles only shows a very small temperature effect due to the fact that the dominant electronic dephasing mechanism involves electron-electron interactions rather than electron-phonon coupling.[14–16] Thus, it is believed that the significant shift of λ_{SPR} originates from the change in dielectric constants of the supporting material VO_2.

The influence of Ag mass thickness d_m on λ_{SPR} seems to be very pronounced, as shown in Fig. 1. An increase in d_m not only leads to a redshift of λ_{SPR} for both of the semiconductor and metal phases but also enlarges the difference in λ_{SPR}, namely, $\Delta\lambda_{SPR}$ between the two phases. For the case of $d_m = 2$ nm, for example, the SPR wavelength λ_{SPR} locates at 650 nm for the semiconductor phase and at 600 nm for the metal phase, with a difference $\Delta\lambda_{SPR} = 50$ nm. In contrast, for the case of $d_m = 8$ nm, λ_{SPR} locates at 780 and 660 nm for the two phases, respectively, with $\Delta\lambda_{SPR} = 120$ nm. When d_m increases further, λ_{SPR} redshifts more, and $\Delta\lambda_{SPR}$ becomes much larger as well with the largest value of $\Delta\lambda_{SPR}$ being 250 nm obtained for $d_m = 10$ nm. The redshift of λ_{SPR} with increasing d_m is attributed to the dipole-dipole interaction of the particles.[1] Such interaction becomes more significant if

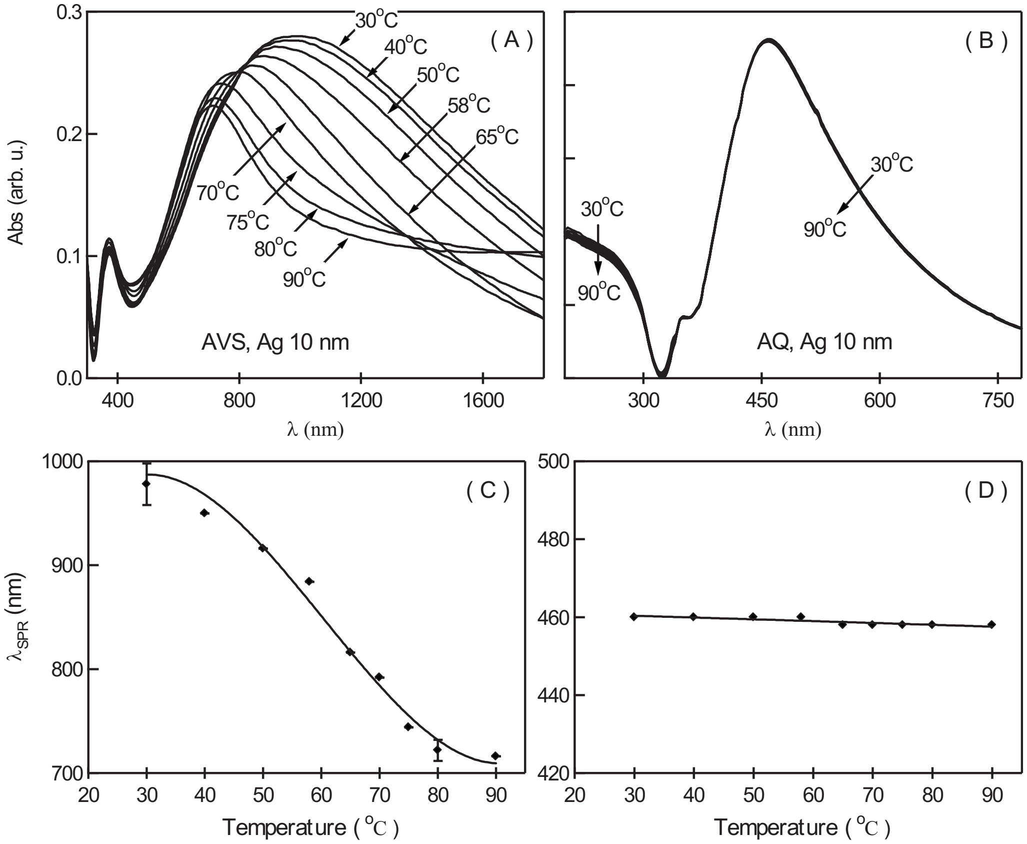

FIG. 2. Tuning of the LSPR band for (a) the AVS and (b) the AQ samples by increasing temperature from 30 to 90 °C in a stepwise manner. The resonance wavelength shifts with temperature in case of (c) the AVS and (d) the AQ samples. The Ag mass thickness is 10 nm.

the particles become larger and the interparticle spacing becomes shorter, which is the case for a natural growth of metal nanoparticles, e.g., thermal evaporation or sputtering, when metal mass thickness inceases.[21] The enlargement in $\Delta\lambda_{SPR}$ results from the increasing difference in dielectric function between the two phases of VO_2 as wavelength increases.[21]

It is worthy to note in Fig. 1 that a subpeak located at around 390 nm is always present in all of the absorbance spectra. Its position is fixed neither shifting with temperature nor with Ag mass thickness. This is quite distinct from resonance properties of noble metal nanoparticles contributed by dipole and/or quadrupole interactions. Additionally, it can be seen that the LSPR absorbance band in the IR region for the metal phase has an upward tail. Although the spectrum of the VO_2/sapphire substrate was taken as a reference during the measurement, we believe that all of these spectral features are caused by the supporting material (VO_2) of the particles. A similar phenomenon was observed when Ag nanoparticles were deposited on indium tin oxide-coated glass.[27] Based on effective medium theory, we demonstrated that the dielectric properties of the substrates have marked effects on the spectral line shape of LSPR; beyond the plasmon resonance band, the spectral shape is predominantly governed by the dielectric function, particularly its imaginary part, of the substrate. This implies that the effect of the substrate *cannot* be excluded even when using a substrate as the reference, in particular the substrate being strongly absorbing. Actually, it is easy to find that the imaginary part $\varepsilon_2(\lambda)$ (Ref. 21) of the

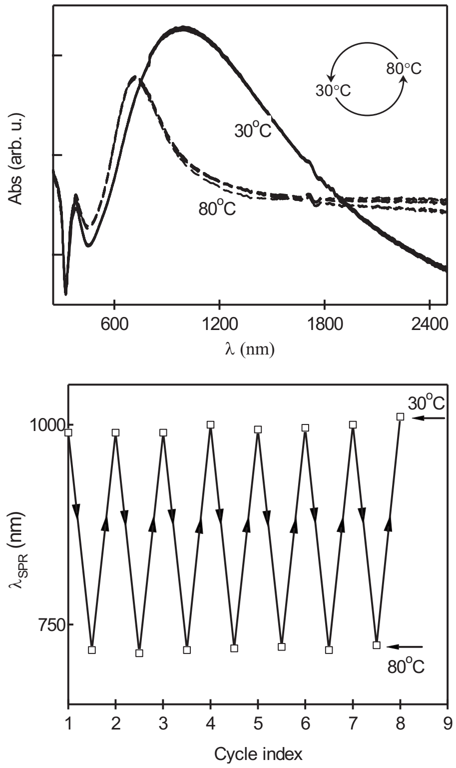

FIG. 3. Absorbance spectra of an AVS sample ($d_m = 10$ nm) measured at 30 and 80 °C under the repetitions of heating-cooling cycle (upper part) and the corresponding location of the resonance wavelength at each cycle (bottom part).

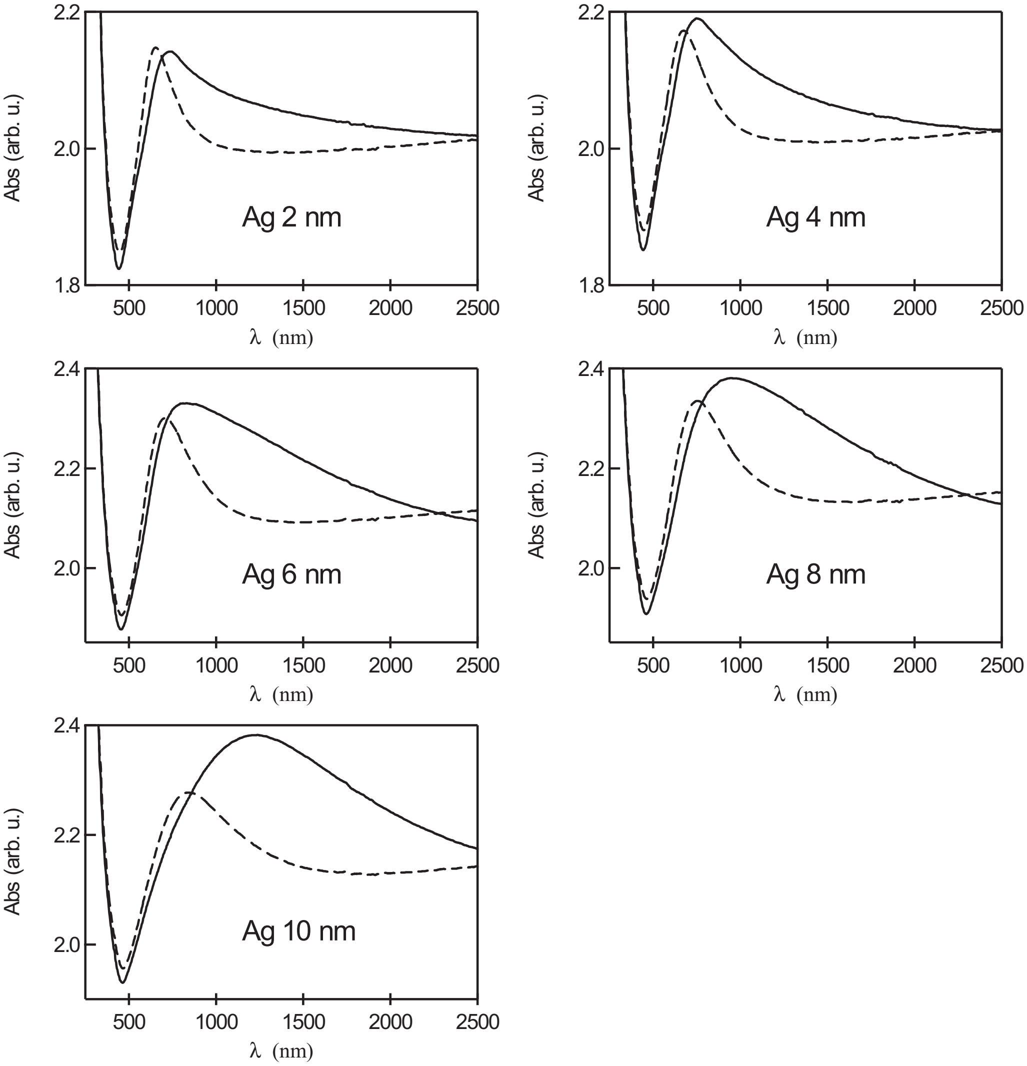

FIG. 4. Absorbance spectra of the TAVS samples with various Ag mass thicknesses for both of the semiconductor (solid curves) and the metal (dashed curves) phases.

dielectric function of VO_2 exhibits the same spectral feature as what we observed in Fig. 1.

The phase transition of VO_2 in the form of thin film is usually smeared out over a broad temperature interval rather than a sharp change at 68 °C for the bulk.[28] Correspondingly, a gradual change in the optical constants (dielectric function or complex refractive index) of VO_2 thin film was observed with increasing or decreasing temperature.[29] Based on this fact a smart tuning of the temperature-dependent shift in λ_{SPR} can be fulfilled. Figure 2(a) shows such a measurement for the AVS sample with $d_m = 10$ nm. In this test the temperature was increased from 30 to 90 °C in a stepwise manner. In this case λ_{SPR} gradually blueshifts against temperature, as shown in Fig. 2(c). For comparison, a similar measurement was performed for the AQ sample also with $d_m = 10$ nm. As expected, the LSPR peak in this case hardly shifts with temperature increasing. The results were plotted in Figs. 2(b) and 2(d).

We further found that the shift in λ_{SPR} is stable and reversible with correspondence to temperature from the measurement of absorbance spectrum with many repetitions of heating-cooling cycle, as shown in Fig. 3. For instance, repeating the temperature cycle between 30 and 80 °C resulted in λ_{SPR} shifting reversibly between 980 and 720 nm. Such a stable and reversible behavior of LSPR is right in accordance with the phase transition characteristics of VO_2 under temperature stimulation,[18–20] suggesting again the origin of the thermal tunability of plasmon resonance of nano-Ag.

It has been demonstrated that the introduction of an external medium makes a dramatic effect on the resonance of Ag nanoparticles,[11] other than the thermochromic material VO_2 being discussed here. In order to gain more insight into the tunability, we used a dielectric layer TiO_2 to overcoat the nano-Ag both for wavelength tuning and for protection of Ag surface from photochemical degradation caused by absorbed species. Figure 4 shows the absorbance spectra of the TAVS with various Ag mass thicknesses ($d_m = 2$, 4, 6, 8, and 10 nm). The solid curves show the results measured at 30 °C, while the dashed curves at 80 °C correspond to the semiconductor and metal phases of VO_2, respectively. Similar to Fig. 1, the resonance wavelengths λ_{SPR} of the TAVS samples also shift to the blue when temperature is increased from 30 to 80 °C, and the difference in λ_{SPR} between the two phases, $\Delta\lambda_{SPR}$, increases with Ag mass thickness. However, the ab-

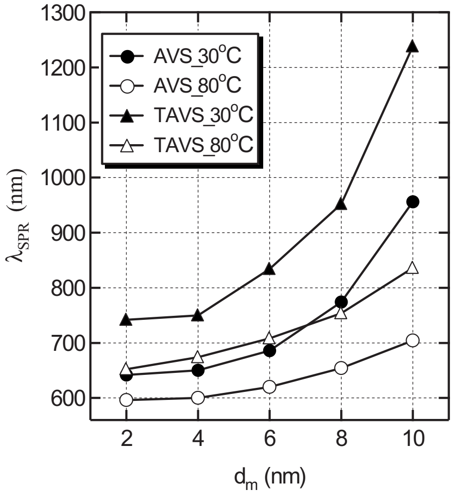

FIG. 5. Dependence of the resonance wavelength λ_{SPR} on Ag mass thickness d_m for the two series of samples, AVS and TAVS, measured at 30 and 80 °C, respectively.

sorbance subpeak at 390 nm disappears because the strong interband absorption of TiO_2 occurs at $\lambda < 400$ nm and covers up the relatively weak absorption from VO_2.

Alhough the major spectral features of the TAVS sample are similar to those of the AVS, the effects of TiO_2 on the tuning of λ_{SPR} are more significant. In Fig. 5, we summarize the dependence of λ_{SPR} on Ag mass thickness for the two series of samples based on Figs. 1 and 4. Note that at the same measuring temperature of 30 or 80 °C, the curves for the TAVS sample lie above those for the AVS, suggesting an extra redshift in λ_{SPR} caused by the addition of TiO_2. Further, we surprisingly find that $\Delta\lambda_{SPR}$ for the TAVS sample with $d_m=10$ nm reaches up to about 400 nm. This value is much larger than the similar case for AVS, a value of about 250 nm. In fact, the TAVS sample at each d_m always has a larger value of $\Delta\lambda_{SPR}$ than the AVS sample does, as shown in Fig. 5. These results demonstrate the positive effects of the addition of TiO_2, which not only leads to a redshift in λ_{SPR} but also greatly enhances the wavelength tunability. The enhancement results from the increasing difference in dielectric functions,[21] specifically their real parts, between the two phases of VO_2 as wavelength increases.

The shift in λ_{SPR} varying with the dielectric environment of the nanoparticles can be described in terms of sensitivity factor.[30,31] This factor is defined as $\Delta\lambda_{SPR}/\Delta n$, in which $\Delta\lambda_{SPR}$ is the resulting wavelength shift by the change in refractive index Δn of the surroundings. If we assume a nanoparticle sitting on a substrate, the surrounding dielectric function ε contains the two contributions from the substrate (ε_{sub}) and the external medium (ε_{ext}). In a simple manner, $\varepsilon=n^2=(\varepsilon_{ext}+\varepsilon_{sub})/2$.[32–34] For our AVS samples, ε_{ext} is unity because the external medium is air and hence $\varepsilon=(1+\varepsilon_{VO_2})/2$, in which ε_{VO_2} is the dielectric function of VO_2. When the external medium of TiO_2 was added to form the TAVS samples, thus $\varepsilon=(5.76+\varepsilon_{VO_2})/2$, the dielectric constant of TiO_2 is taken into account. Based on these definitions, the sensitivity factors for the two phases of VO_2 can be calculated. The results were plotted in Fig. 6. As seen in the figure, the sensitivity factor generally increases with Ag mass thickness d_m for both of the two phases of VO_2 and a value, as large as 478 nm/refractive index unit, was obtained for the semiconductor phase at $d_m=10$ nm. Such a large value means that the AVS sample is highly sensitive to the dielectric environment and may be used in nanoscale optical sensors.

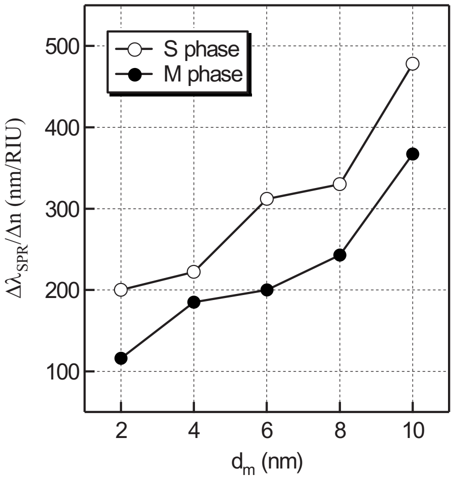

FIG. 6. Sensitivity factor as a function of Ag mass thickness d_m for the AVS sample at the semiconductor (s) and metal (m) phases.

IV. CONCLUSIONS

In conclusion, we have studied in detail the SPR tunability of Ag nanoparticles on a thermochromic thin film of VO_2. The resonance can be tuned thermally and is reversibly tunable in a wide spectral region due to the temperature-dependent dielectric properties of VO_2. By controlling the temperature in a stepwise manner, the resonance wavelength can be fine tuned. Larger Ag nanoparticles or particle films with larger mass thickness make the tuning more pronounced and effective. The wavelength tunability can be further improved by combining TiO_2 and VO_2 as the surrounding dielectric medium of the nanoparticles. Additionally, it is demonstrated that Ag nanoparticles on VO_2 possess a very high sensitivity to the external dielectric environment surrounding the particles. These results are expected to stimulate extensive research pertinent to the nanometal-VO_2 composite systems for their potential usage in temperature-sensitive nanophotonics, nanosensor, and so on.

Our study actually opens a new way to manipulate the LSPR of meal nanoparticles characterized by large tunable wavelength range, thermal reversibility, and capability of fine tuning. Note that such tuning is activated by the change in refractive index of VO_2 with temperature. We can modify the thermochromism of VO_2 or use other thermochromic materials to tune the resonance for a wider spectral response or at a different temperature region.

ACKNOWLEDGMENTS

This work was supported by the National High Technology Research and Development Program of China (Grant Nos. 2007AA03Z326 and 2007AA05Z431) and the Bureau of Science and Technology of Guangzhou Municipality (Grant No. 2007Z2-D2051).

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