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# Abnormal thermal effects on the surface plasmon resonance of Ag nanoparticles on the surface of silicon

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ABSTRACT

The thermal effects on the surface plasmon resonance (SPR) of Ag nanoparticles on the silicon surface have been studied. It is found that unusual blue shifts and narrowing of the SPR troughs occur as the temperature increases from 323 K to 363 K. At low temperature range (from 273 K to 323 K), the SPR troughs have the normal red shifts and broadening as in previous studies. The change of SPR is attributed to the thermal induced electron transport between particles and substrate, and is analyzed using samples with different particle sizes. This work reveals the mechanism of thermal effects on the plasmonic properties of Ag nanoparticles on the surface of silicon and offers useful information for designing of SPR devices.



## 1. Introduction

In the past few years, the plasmonic properties of noble metal nanoparticles have been used in the thermal cancer treatment [1,2], nanostructure growth [3], and computer chips [4]. The remarkable optical properties of noble metal nanoparticles in these devices can be attributed to the surface plasmon resonance (SPR) phenomenon [5,6]. In previous studies, noble metal nanoparticles were generally embedded inside the host material. The amplitude and frequency of the SPR can be changed with temperature, which is well known as the thermo-plasmonic properties of metal nanoparticles [7]. In general, the noble metal nanoparticles are directly deposited on the surface of the semiconductor substrate in lots of real devices such as some solar cells and sensors [8–10]. However, the thermal effects on the plasmonic properties of noble metal nanoparticles deposited on the semiconductor surface are much more complex in contrast to the metal nanoparticles embedded in a host material in previous studies. Therefore, it is quite desirable to investigate the thermal effects on the SPR of noble metal nanoparticles deposited on the surface of semiconductor substrate.

In this paper, we have studied the thermal effects on the SPR of Ag nanoparticles deposited on the silicon surface. As temperature increases to 363 K, unusual blue shifts and narrowing of the SPR troughs are observed. This unusual phenomenon is demonstrated by the Thermionic-emission, Mie theories and Drude model to reveal the mechanism of the changes of SPR trough. Theoretically, a possible mechanism of thermal effects on the SPR for the Ag nanoparticles on the silicon surface is discussed. This work is useful for the design of some SPR devices.

## 2. Experimental details

Ag nanoparticles are fabricated on the silicon surface for optical reflection measurements. One-side polished p-type Si (100) wafers with thickness around 0.5 μm are chosen for their high conductivity and good optical thermal stability. Ag nanoparticles with different particle sizes are deposited on the silicon surface by the sputter-anneal process. The sizes of Ag nanoparticles are controlled by varying sputter current. All sputtering processes are sustained 30 s with the sputter current ranging from 10 mA to 25 mA to deposit Ag thin layers onto the silicon surface. Then, the annealing processes are carried out in nitrogen at the temperature of 673 K for 2.5 h to coalesce the flat layers together to form nanoparticles with certain average particle sizes. Three types of samples are fabricated: C10, C15, and C25 which correspond to the different sputter current mentioned above.

The sputtering of Ag layers is completed using Quorum Q150TS. The surface reflectance (300–700 nm) is measured by Solar Cell Quantum Efficiency/Incident Photon-to-Electron Conversion Efficiency Measurement System at the temperatures of 273 K, 323 K and 363 K. The morphology of Ag nanoparticles is characterized by using scanning electron microscopy (Model FEI Quanta 200 F) which is made in Holland. The operating voltage used in the measurement is 30 kV. The size distributions and the average particles sizes are counted by *ImageJ* software (Version 1.43b, Published by National Institutes of Health, U.S.A.).

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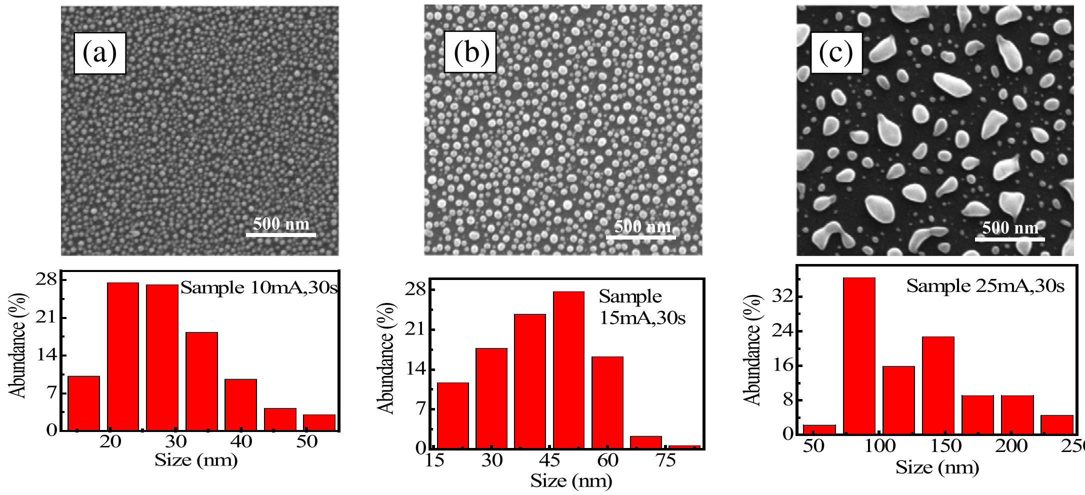


**Fig. 1.** SEM images with corresponding size distribution histograms of Ag nanoparticles on the silicon substrate; samples (a) C10 and (b) C15 and (c) C25.

## 3. Results and discussion

As previous studies, the plasmonic properties of Ag nanoparticles depend on the damping effects which can be divided into two mechanisms: surface damping effect and radiation damping effect [5]. These two mechanisms in turn greatly depend on the particle size and the surrounding permittivity [11]. Normally, the plasmonic properties can mainly be attributed to the surface damping effect which often leads to the light absorption, while the particle sizes are smaller than 50 nm [12,13]. For the particle sizes larger than 50 nm, the radiation damping effect domains the plasmonic properties of Ag nanoparticles, which exhibits strong forward scattering surrounding Ag nanoparticles [14,15]. Ag nanoparticles with three kinds of average particle size which could cover the two mechanisms are chosen in order to distinguish the influence of thermal effects on these two mechanisms, shown in Fig. 1(a), (b) and (c). The diameters of the particles are estimated for different samples as: sample C10 (<d> = 30 nm), C15 (<d> = 50 nm) and C25 (<d> = 150 nm) and all the nanoparticles are isolated and have spherical shape. Also, SEM results reveal large gaps exceeding the particle sizes between these nanoparticles.

Taking into consideration the effects of low melting temperature (could be lower than 473 K) and the possible oxidation of Ag nanoparticles (occur at 398 K) on the experiment [11,16], the temperatures ranging from 273 K to 363 K are chosen. The diffuse reflectance spectra of the samples are measured at the temperature of 273 K, 323 K and 363 K so as to determine the thermal effects on the plasmonic properties of Ag nanoparticles on the silicon surface, as shown in Fig. 2. The insert in Fig. 2 reveals the local enlarging graphs of each wave trough in the SPR frequency range.

As shown in Fig. 2(b) and (c), obvious red shifts and broadening of wave troughs are observed at 323 K. Furthermore, blue shifts of SPR are observed while the temperature further increase to 363 K and this is unusual. In these two wave troughs, the obvious red shifts are observed about 5 nm and 22 nm, and the blue shifts are about 7 nm and 28 nm, respectively. The obvious wave troughs in Fig. 2(b) and (c) can be attributed to the damping effects of Ag nanoparticles [5]. The little wave troughs are caused by the light absorption of surface damping effect for the small particle size as shown in Fig. 2(a). The obvious reduction of the diffuse reflectance in Fig. 2(b) and (c) can mainly be attributed to the radiation damping effects of larger Ag nanoparticles. However, the plasmonic shifts and width changes with temperature can only be obviously observed in Fig. 2(b) and (c). For the obvious shifts and width changes of the SPR of larger Ag nanoparticles, it is concluded that the radiation damping effect of Ag nanoparticles on the silicon surface is much more sensitive to temperature.

As reported previously, the radiation damping effect can be affected by the injected or exported hot electrons in Ag nanoparticles which would lead to reduction or enhancement of the radiation damping effects [10,14]. The change of the damping effects would lead to the shifts and width changes of the SPR [17–19]. Thus, in the present work, the thermal effects on the radiation damping effect are studied through the electron transport mechanism between Ag nanoparticles and silicon substrate. In the process of depositing Ag nanoparticles on silicon surface through sputtering and annealing, Schottky junctions can be

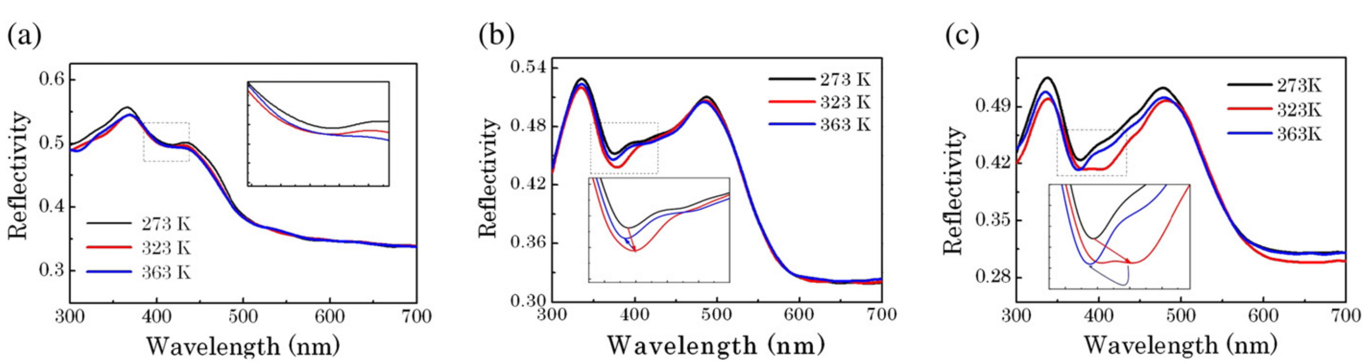


**Fig. 2.** The diffuse reflectance spectra of silver nanoparticles with average particle size (a) 30 nm, (b) 50 nm and (c) 150 nm on the silicon surface at the temperature of 273 K, 323 K and 363 K.

formed in the samples for the direct contacts between Ag nanoparticles with the silicon substrate [10]. The electron emitting rate of these Schottky junctions is affected by the temperature. The relationship between the electron emitting rate and temperature is shown as follow [20]:

$$I_{sat} = SA^{**}T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \tag{1}$$

where $S$ is the Schottky contact area, $q\phi_B$ is the barrier height, $A^{**}$ is the reduced effective Richardson constant, $T$ is the operating temperature in Kelvin, and $k$ is Boltzmann's constant. Clearly, in Eq. (1), the emitting rate increases with temperature. This effect slightly reduces the electron density in Ag nanoparticles and will lead to an enhancement of the radiation damping effects of Ag nanoparticles which exhibit the obvious red shift and broadening of wave troughs from the temperature 273 K to 323 K as shown in Fig. 2(b) and (c). Furthermore, the radiation damping can be enhanced as well as increase in particle sizes [12]. Thus, the radiation damping effect on Ag nanoparticles with larger particle sizes is more temperature sensitive than the smaller ones, and leads to the larger shifts and broader SPR trough, as revealed in Fig. 2(c).

In this study, the unusual blue SPR shift can be attributed to the electron tunneling effect caused by the increment of the e–h pairs in silicon substrate at high temperature. The electron tunneling screens the capacitive effect of the Schottky junctions. This screen effect causes the electrons to flow back and leads to a slight incensement of the electron density in Ag nanoparticles. The incensement of the electron density in Ag nanoparticles leads to an attenuation of the radiation damping effects [19] and exhibits the blue shift and narrowing of SPR trough in Fig. 2(b) and (c). Therefore, as temperature is increased further, the shifts and width changes of the SPR troughs can be attributed to the influence of electron transport on the radiation damping effects of Ag nanoparticles.

The optical properties of the material can be changed by changing of temperature, such as the thermal irreversible morphology change [21], thermal expansion, and permittivity changes of Ag nanoparticles [6]. Thus, these important factors of material should be carefully scrutinized.

In order to directly scrutinized the morphology changes of Ag nanoparticles deposited on silicon substrate, SEM images of Ag nanoparticles before and after thermal treatment are presented in Fig. 3(a) and (b). It can be clearly observed that no obvious changes of Ag nanoparticles can be found before and after thermal treatment in these images. In addition, diffused reflectance test of above sample was carried out by increasing the temperature from 273 K to 363 K, and then reducing back to 273 K. As shown in Fig. 4, the diffused reflectance is recovered as the temperature reduced back, which further proves that no irreversible morphology change occurs in range of 273 K to 363 K.

Then, the established thermo-dependent Drude model was adopted to reveal the thermal response of the permittivity of Ag nanoparticles

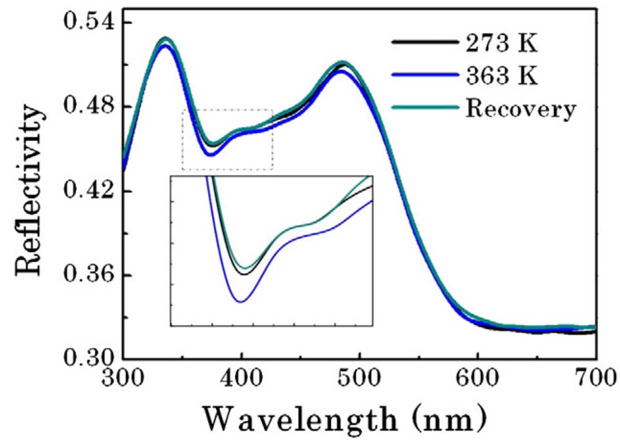


**Fig. 4.** Diffuse reflectance spectra of the sample under cycle tests; the dark cyan line describes the reflectance under temperature reducing back to 273 K.

for the dependence of the optical properties of the metal on its permittivity, in which the thermal effect on the electron–electron, electron–phonon scattering rate and thermal expansion of Ag nanoparticles has been considered [6]. Through our calculation, we found that the imaginary part permittivity of Ag $\varepsilon_i$ had 8.3% enlargement and the real part $\varepsilon_r$ had about 1.0% enlargement from 273 K to 363 K around SPR. Mie theory is used to evaluate this response on the diffused reflectance for its accurate description of the optical properties of nanoparticles. The temperature variation of Ag permittivity is introduced into extinction cross section $C_{ext}$ [14]. Near the SPR, due to $\varepsilon_r = -2\varepsilon_m$, the expression of $C_{ext}$ can be simplified as:

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda|\varepsilon_i|} \tag{2}$$

where $R$ is the radius of particle, and $\varepsilon_m$ is the relative dielectric constant of the medium surrounding the particle. When $\varepsilon_i$ increases, the extinction cross section reduces, and leads to a slight increase in diffused reflectivity near the SPR position. The calculation results indicate that no obvious shifts of SPR trough would occur because of the slight change of $\varepsilon_r$ with increase in temperature, which is obviously incompatible with the observations. From the foregoing, it is clear that the thermal effects have little direct impact on shifts and width changes of Ag nanoparticles within the temperature range from 273 K to 363 K. The changes of SPR can be mainly attributed to the thermal induced electron transports between Ag nanoparticles and substrate. From this study, the revelation of the mechanism could possibly provide us useful information to improve the thermal stability of SPR devices.

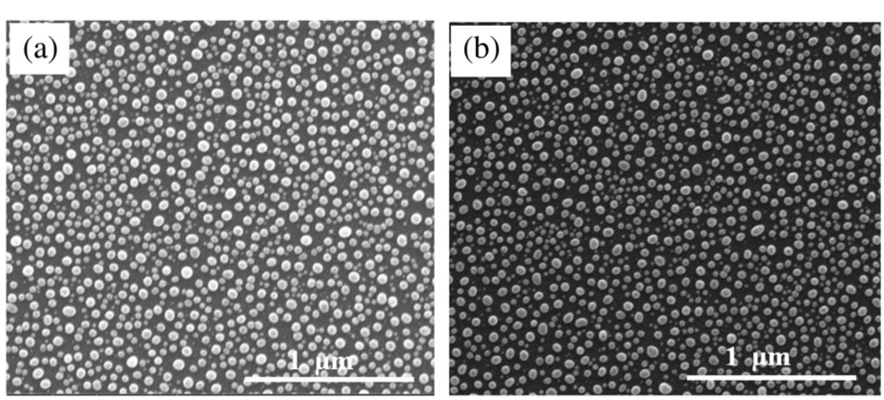


**Fig. 3.** SEM images of Ag nanoparticles deposited on silicon substrate in one sample. (a) Before thermal treatment; (b) after thermal treatment.

## 4. Conclusion

The thermal effects on the SPR of Ag nanoparticles with different particle sizes on the silicon surface have been studied. Through mathematical and theoretical analysis, for the particle sizes larger than 50 nm, the results reveal that obvious shifts and width change of the SPR troughs are mainly caused by the impact of electron transports on the radiation damping effect. Furthermore, the possible thermal effects on the morphology change and the damping effects of Ag nanoparticles itself have been studied. The results reveal that the thermal effects have slight effects on Ag nanoparticles. This study presents some useful information for designing of SPR devices.

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## References

[1] D. O'Neal, L. Hirsch, N. Halas, J. Payne, J. West, Photo-thermal tumor ablation in mice using near infrared-absorbing nanoparticles, Cancer Lett. 209 (2004) 171.
[2] L. Cao, D.N. Barsic, A.R. Guichard, M.L. Brongersma, Plasmon-assisted local temperature control to pattern individual semiconductor nanowires and carbon nanotubes, Nano Lett. 7 (2007) 3523.
[3] W. Cai, J.S. White, M.L. Brongersma, Compact, high-speed and power-efficient electrooptic plasmonic modulators, Nano Lett. 9 (2009) 4403.
[4] L.G. Grechko, A.O. Pinchuk, A. Lesjo, Absorption of far-infrared radiation by metal-dielectric composites, Proc. SPIE Int. Soc. Opt. Eng. 3890 (1999) 149.
[5] U. Kreibig, M. Vollmer, Optical Properties of Metal Clusters, Springer, Berlin, 1995.
[6] M.R. Huyeh, M.S. Havar, B. Palpant, Thermo-optical properties of embedded silver nanoparticles, J. Appl. Phys. 112 (2012) 103101.
[7] O.A. Yeshchenko, I.M. Dmitruk, A.A. Alexeenko, A.V. Kotko, J. Verdal, A.O. Pinchuk, Size and temperature dependence of the surface plasmon resonance in silver nanoparticles, Ukr. J. Phys. 57 (2012) 266.
[8] H.P. Chiang, C.W. Chen, J.J. Wu, H.L. Li, T.Y. Lin, E.J. Sánchezc, P.T. Leungc, Effects of temperature on the surface plasmon resonance at a metal–semiconductor interface, Thin Solid Films 515 (2007) 6953.
[9] C. Eminian, F.J. Haug, O. Cubero, X. Niquille, C. Ballif, Photocurrent enhancement in thin film amorphous silicon solar cells with silver nanoparticles, Prog. Photovolt. Res. Appl. 19 (2011) 260.
[10] J.H. Werner, H.H. Güttler, Temperature dependence of Schottky barrier heights on silicon, J. Appl. Phys. 73 (1993) 1315.
[11] H. Dai, M.C. Li, Y.F. Li, Hang Yu, Fan Bai, Xiaofeng Ren, Effective light trapping enhancement by plasmonic Ag nanoparticles on silicon pyramid surface, Opt. Express 20 (2012) A502.
[12] B. Lamprecht, A. Leitner, F.R. Aussenegg, SHG studies of plasmon dephasing in nanoparticles, Appl. Phys. B 68 (1999) 419.
[13] A. Melikyan, H. Minassian, On surface plasmon damping in metallic nanoparticles, Appl. Phys. B 78 (2004) 453.
[14] C.F. Bohren, D.R. Huffman, Absorption and Scattering of Light by Small Particle, Wiley, New York, 1998.
[15] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment, J. Phys. Chem. B 107 (2003) 668.
[16] Q. Xiang, G.F. Meng, Y. Zhang, J.Q. Xu, P.C. Xu, Q.Y. Pan, W.J. Yu, Ag nanoparticle embedded-ZnO nanorods synthesized via a photochemical method and its gas-sensing properties, Sensors Actuators B Chem. 143 (2010) 635.
[17] S.C. Warren, D.A. Walker, B.A. Grzybowski, Plasmoelectronics: coupling plasmonic excitation with electron flow, Langmuir 28 (2012) 9093.
[18] S. Linic, P. Christopher, D.B. Ingram, Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy, Nat. Mater. 10 (2011) 911.
[19] H. Choi, W.T. Chen, P.V. Kamat, Know thy nano neighbor. Plasmonic versus electron charging effects of metal nanoparticles in dye-sensitized solar cells, ACS Nano 6 (2012) 4418.
[20] M.W. Knight, Y.M. Wang, A.S. Urban, A. Sobhani, B.Y. Zheng, P. Nordlander, N.J. Halas, Embedding plasmonic nanostructure diodes enhances hot electron emission, Nano Lett. 13 (2013) 1687.
[21] K.K. Nanda, S.N. Sahu, S.N. Behera, Liquid-drop model for the size-dependent melting of low-dimensional systems, Phys. Rev. A 66 (2002) 013208.