The edges and terrace effect of Ag particles on optical resonance absorption property*

Zhao Ya-Li(赵亚丽)[a)†], Gui Ya-Qiang(桂亚强)[a)], Zhang Zhen-Lin(张振林)[a)], Ma Fu-Hua(马富花)[a)], Xu Xiao-Li(许晓丽)[a)], and Xu Xiao-Liang(许小亮)[b)]

[a)] *The 33rd Institute of Branch, China Electronics and Technology Corporation, Taiyuan* 030006, *China*

[b)] *Structure Research Laboratory, University of Science and Technology of China, Hefei* 230026, *China*

(Received 10 March 2011; revised manuscript received 29 April 2011)

Alternative Ag and SiO_2 multilayers are prepared by using radio frequency magnetron sputtering. The Ag particles are found to diffuse toward and mostly accumulate near the surface of the Ag–SiO_2 composite film via a rapid thermal treatment. Different shapes of the Ag particles are obtained by changing the thickness of each Ag and SiO_2 layer. The response absorption property of the Ag composite film is also investigated. We relate the resonance absorption to the surface level and the Fermi level. To induce the obvious resonance absorption in an Ag composite film, it is necessary to maintain special shapes with sharp edges and wide terraces and to maintain the particle sizes ranging from 0 nm to 100 nm.

Keywords: resonance absorption, edges and terrace, surface state, Fermi level

PACS: 73.20.Mf, 78.67.Bf **DOI:** 10.1088/1674-1056/20/9/097301

1. Introduction

Nanocomposite films consisting of metal particles, such as Au, Ag, Cu, and Al, provide great potential for future optoelectronic applications. The induced surface-plasmon resonance (SPR) of the metal particles is responsible not only for a strong absorption band, but also for the strong enhancement of the local electric field.[1,2] The magnitude of the enhancement factor is almost 10^{14}.[1,2] Since the volume of the high enhancement is limited to a few nanometers between the Ag particles,[3] only particles near the surface play a role for the enhancement.

As demonstrated in last decades, the Ag–SiO_2 and other composite films, in which most Ag particles are embedded inside the dielectric matrices, have been grown by using physical techniques.[4−11] It is impossible to use the localized energy due to the confinement of the local field. In our work, after preparing the Ag/SiO_2 multilayer, the Ag nanoparticles diffuse towards and mostly accumulate near the surface of the composite film via a rapid thermal treatment. We have shown the process of the rapid thermal treatment in a previous paper.[12] In the present paper, Ag nanoparticles of dissimilar shapes are obtained by changing the thickness of each Ag and SiO_2 layer and the annealing time. By investigating the response absorption, we set up a bridge between the surface state and the optical properties of the Ag nanoparticles. We find that not all Ag nanoparticles but only those that have sharp edges and wide terraces are able to exhibit obvious response absorption. It is important to deny the previous statement[3] that the response absorption certainly happens as long as the size of the particles is small enough.

2. Experimental details

In our work, the Ag and the SiO_2 layers of the films were alternatively prepared by using magnetron sputtering. The Ag particles were found to diffuse toward the surface during the thermal treatment. Both the silver and the SiO_2 targets (4N) were sputtered intermittently in argon plasma in a vacuum chamber at a pressure of 3 Pa. The films were grown on a glass substrate at ambient temperature. The base pressure was 5×10^{-4} Pa. The radio frequency (RF) powers for growing Ag and for growing SiO_2 were 20 W and 80 W, respectively. The corresponding growth rates were 60 Å/min and 8 Å/min, respectively. Different Ag particles were fabricated by changing the thickness

*Project supported by the National Natural Science Foundation of China (Grant No. 50872129) and the National Basic Research Program of China (Grant No. 2006cb302900).

†Corresponding author. E-mail: yaliz12@163.com

© 2011 Chinese Physical Society and IOP Publishing Ltd

of each Ag and SiO_2 layer. The growth parameters of the samples are listed in Table 1.

Table 1. Growth parameters of Ag/SiO_2 samples.

Sample	1	2	3	4
(Ag, SiO_2) thickness/nm	(1, 5)	(2, 4)	(2, 10)	(4, 20)
Runs	4	4	2	1

Thermal annealing was performed in the nitrogen atmosphere, and the heating rate was 100 °C/s. All samples were annealed at 500 °C. The annealing time was obtained from the following formula:

$$T = d \times 7/4 \text{ (min)}, \tag{1}$$

where d is the thickness (nm) of each SiO_2 layer and 7/4 nm·min^{-1} corresponds to the diffusion speed of the Ag particle in the SiO_2 matrix. The annealing temperature and the annealing time were determined by the experiment in our previous work.[12]

3. Results and discussion

3.1. Generation of nanoparticles with different morphologies

The images of the Ag particles in the composite films were obtained by using atomic force microscopy (AFM), and their size distribution was obtained by analysing the individual Ag particles in the AFM images. The optical absorption spectra of the Ag–SiO_2 films were measured in a range of 300–800 nm with a resolution of 1 nm.

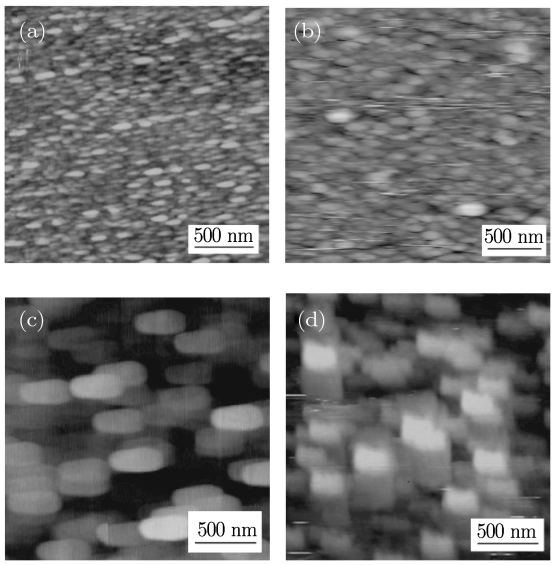


Fig. 1. AFM images of samples 1 (a), 2 (b), 3 (c), and 4 (d).

The AFM images of samples 1, 2, 3 and 4 are shown in Figs. 1(a)–1(d), respectively. On one hand, if the annealing time remains unchanged, there is no obvious increase in the particle size with the increase of the thickness of each Ag layer, as shown in sample 2 compared with sample 1 (see Figs. 1(a) and 1(b), a detailed explanation is to be given in Figs. 2(a) and 2(b) below). However, the particle density obviously increases and the aspect ratio a/b significantly decreases. On the other hand, a comparison of sample 3 with sample 2 (see Figs. 1(b) and 1(c)) shows that if the thickness of each Ag layer is kept at 2 nm and the annealing time is changed, particle size increases prodigiously with the increase in annealing time, while the density decreases to a considerable extent. The particle size mostly depends on the Ag particle diffusion length. As the annealing time increases, particles form a facet parallel to the substrate (as shown in Fig. 1(c)), atoms could easily migrate on the facet. Thus the particles tend to be in a critical size namely, the particle size distribution departs from the Gauss distribution (as shown in Fig. 2(c)), and the Ag particle is stable in that situation.

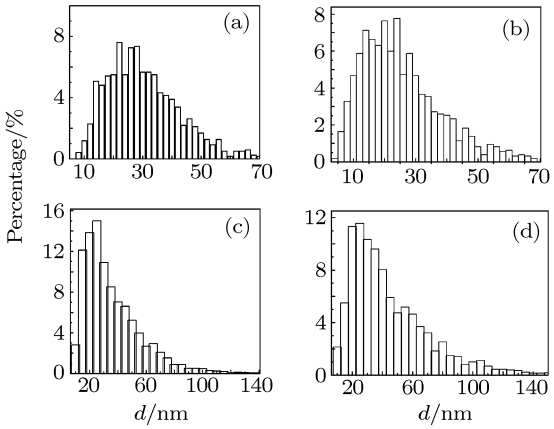


Fig. 2. Size distributions of Ag particles for samples (a) 1, (b) 2, (c) 3, and (d) 4.

Another phenomenon is also found in our work. Despite of the increase in the thickness and in the diffusion length of Ag with respect to those of sample 3, there is no considerable increase in size for sample 4. The reason for this is given below.

As for the limitation aggregation on the facet, the only way for particle amalgamation is if the whole particle jumps onto facets of other particles. The special amalgamation is clearly shown in Fig. 3. As a result of all particles being approximately the same size and the random movement of the top particles, the boundary of the top particles probably turns close to or goes out of the bottom boundary, especially for the edges of

the particle. According to the theory given by Giesen *et al.*,[13] the Enrlich–Schwoebel barrier (ESB) for the interlayer mass transport vanishes for $w < w_c$, where w is the width of the terrace between two layers in the Ag particle microstructure. The critical width w_c will be explained in the next part. According to the theory, the special amalgamation with facets leads to the easier mass transport, and the edges of the particle can easily decay. Finally, the ellipsoidal shape of the particles turns into the cuboid shape shown in Fig. 1(d).

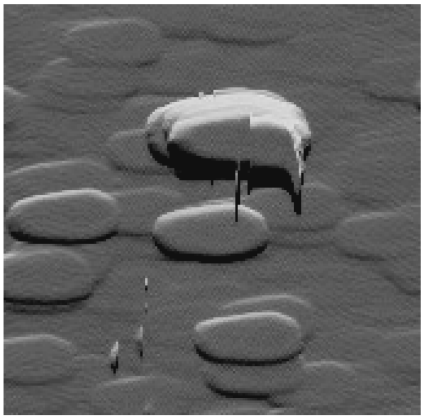


Fig. 3. Image of Ag particles amalgamated.

The phenomenon that the particle size increases with the increase in diffusion length is blocked by the emergence of the facet. Simultaneously, the particle size distribution departs from the Gauss distribution.

3.2. Optical resonance absorption

Here we discuss the relationship between the optical properties and the number of the electrons on the Fermi level (E_F). Under an electromagnetic field, the composite films will exhibit the response absorption and the enhancement of the local electric field. On one hand, the response absorption appears as a result of the hoping of electrons from E_F to the SPR level, therefore the intensity of the response absorption depends mostly on the number of the electrons on E_F.[6] On the other hand, the magnitude of the enhancement is also related to the number of the electrons on E_F. According to the previous work,[14] the enhancement is induced by the charge on the surface of the Ag particle. The larger enhancement is attributed to a larger number of electrons on the surface of the Ag particle. However, only the electrons near E_F can run up to the surface in a weak electromagnetic field,[15] such as that of an optical field. In other words, a large number of electrons in E_F leads to more charge on the surface of a particle in an electromagnetic field. Consequently, a strong enhancement of the local field occurs.

As noted above, both the response and the local enhancement rely mostly on the number of the electrons near E_F. The factors influencing the number of the electrons on E_F will be centralized. It is recognized that the termination of a lattice by a surface gives way to a surface level E_0 formed by new electronic states, whose wave functions are located at the surface.[10] Commonly, E_0 is not equal to E_F. The gap between them can be obtained by using the Kohn–Sham equation,[16]

$$\left\{ -\frac{1}{2}\boldsymbol{\nabla}^2 + V_{\text{eff}}(\rho(r), r) \right\} \varphi_i(r) = E_i \varphi_i(r), \quad (2)$$

$$\rho(r) = 2 \sum_{i}^{\text{occ}} |\varphi_i(r)|^2 n_i, \quad (3)$$

where $\rho(r)$ indicates the electron density, n_i is equal to 1 for an occupied state and 0 for an unoccupied state. The V_{eff} indicates the effective potential and can be obtained from the following equation,[13]

$$V_{\text{eff}}(\rho(r), r) = V(r) + V_{\text{xc}}(\rho(r)), \quad (4)$$

where $V(r)$ is the sum of the electronic potential in the Ag^+ field and the electron Hartree potential, and $V_{\text{xc}}(\rho(r))$ is the exchange–correlation potential of the electron with a density of ρ, which belongs to the chemical potential. Generally, the $V_{\text{xc}}(\rho(r))$ is larger in the bulk than on the surface of the Ag clusters due to the larger electronic density in the bulk. In this situation, electrons will migrate from the bulk to the surface, namely, from E_F to E_0. Hence the new Fermi level E'_F appears, as shown in Fig. 4.[17]

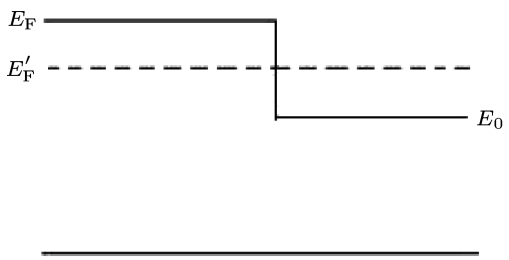


Fig. 4. Energy bands of the metal particle.

For the optical properties we discussed, E'_F corresponds to E_F. The optical properties rely mostly on the number of electrons on E'_F instead of on E_F. The particle sizes of samples 1 and 2 are almost the same, therefore we assume that the numbers of the electrons on their E_F are the same. The number of the electrons on E'_F depends mostly on the occupation status of the surface state and on the gap between E_F and E_0. The

gap is produced by the difference of the electron density between the surface and the bulk according to Eqs. (2)–(4). Generally, the sharper edge of a particle corresponds to the larger difference of the electron density between the surface and the bulk, and more electrons are induced on the $E'_{\rm F}$ level. The theory is well proved by the difference between the resonance absorption spectra of samples 1 and 2.

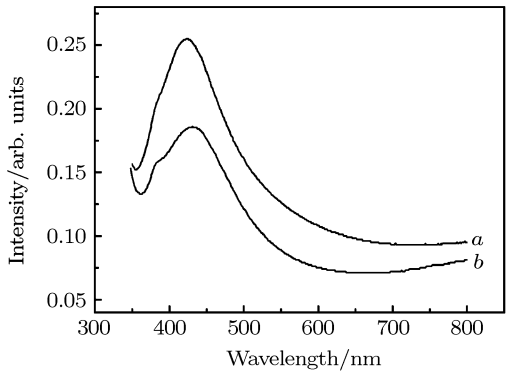


Fig. 5. Absorption spectra of samples 1 (a) and 2 (b).

The intensity of the response absorption obviously decreases for sample 2 compared with that for sample 1, despite the increased density and number of the Ag particles. The phenomenon is due to the sharper edges and the increase of the ellipsoidal-shape Ag particles in sample 1.

To analyse the effect of the terrace between the steps on optical properties, the absorption spectra of samples 3 and 4 were measured. According to the Giesen's theory,[13] a terrace corresponds to a node in the surface state.[13,18,19] Thus, the wave function of a surface state is confined to a narrow terrace between two steps, and the ground state energy of the surface state is pushed up to above $E_{\rm F}$. Hence the occupation of the surface state changes from a maximum value on the large terrace to zero. The critical width $w_{\rm c}$ corresponds exactly to the terrace width below which the surface state is pushed up to above $E_{\rm F}$ due to the quantum confinement. The phenomenon that the occupation of the surface state decreases will lead to the decrease of the number of the electrons on $E'_{\rm F}$. According to the above theory, the intensity of the response absorption is distinctly weakened. The phenomenon is shown in Fig. 6. Although the particle density of sample 4 is increased as compared with that of sample 3, the intensity of the response absorption is contrarily weakened, which results from the narrow terraces in sample 4.

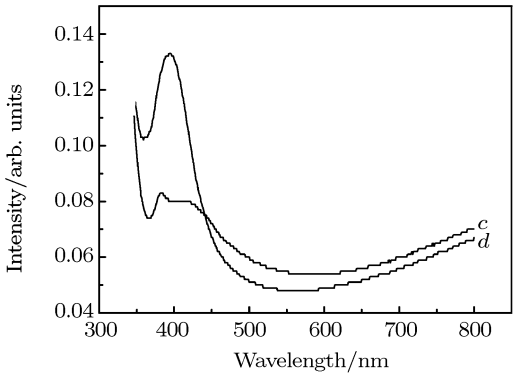


Fig. 6. Absorption spectra of samples 3 (c) and 4 (d).

4. Conclusion

The particle size relies mainly on the diffusion length (the thickness of SiO_2) and the corresponding annealing time. On one hand, the aspect ratio a/b decreases and the density of particles increases, as the thickness of each Ag layer increases. On the other hand, the size of the particle significantly increases and the density relatively decreases before forming facets. Contrarily, the particle size no longer increases with the increase of the diffusion length after the forming of facets on particles. Correspondingly, the size distribution of the Ag particles departs from the Gauss distribution. If the annealing time increases, the ellipsoidal shape of the particles turn into the cuboid shape.

Through investigating the response absorption spectra of all samples, we find that the optical properties are notably related to the surface state, which corresponds to the shapes of the Ag particles near the surface of the film. The particles with sharper edges and wider terraces between steps have stronger intensity of the response absorption. When the width of the terrace is below a critical size $w_{\rm c}$, the intensity is significantly weakened due to the decrease of the occupation of the surface state. To induce the obvious response absorption in an Ag–SiO_2 composite film, it is necessary to keep the particle sizes ranging from 0 nm to 100 nm and to maintain their specific shapes with sharp edges and wide terraces.

References

[1] Blanco L A and Garcia de Abajo F J 2004 *Phys. Rev.* B **69** 205414

[2] Mandal S K, Roy R K and Pal A K 2002 *J. Phys.* D: *Appl. Phys.* **35** 2198

[3] Xu H X, Aizpurua J, Apall P, Aizpurua J and Kall M 2000 *Phys. Rev.* E **62** 4318

[4] Shi Y L, Zhou Q L and Zhang C L 2009 *Chin. Phys.* B **18** 5518

[5] Liu Z X, Wang H H and Li H 1998 *Appl. Phys. Lett.* **72** 1861

[6] Yang L, Li G H and Zhang L D 2000 *Appl. Phys. Lett.* **76** 1537

[7] Liu L J, Yue Y Z and Hao Y 2009 *Acta Phys. Sin.* **58** 536 (in Chinese)

[8] Huang Q, Zhang X D and Zhao Y 2010 *Acta Phys. Sin.* **59** 2753 (in Chinese)

[9] Roy R K, Mandal S K, Bhattacharyya D and Pal A K 2003 *Eur. Phys. J.* B **34** 25

[10] Camelio S, Toudert J, Babonneau D and Girarrdeau T 2005 *Appl. Phys.* B **80** 89

[11] Camelio S, Babonneau D, Giradeau T, Toudert J, Lignou F, Denanot M F, Maitre N, Barranco A and Guerin P 2003 *Appl. Opt.* **42** 674

[12] Zhao Y L, G F, Wang Z B, Ming H and Xu X L 2007 *Acta Phys. Sin.* **56** 3564 (in Chinese)

[13] Giesen M, Schulze Lcking-Konert G and Ibach H 1999 *Phys. Rev. Lett.* **82** 3101

[14] Garcia-Vidal F J and Pendry J B 1996 *Phys. Rev. Lett.* **77** 1163

[15] Wang G H 2003 *Cluster Physics* (Shanghai: Shanghai Scientific and Technical Publishers) p. 87 (in Chinese)

[16] Xie X D and Lu D 1998 *Energy Band Theory of Solids* (Shanghai: Fudan University Press) p. 200 (in Chinese)

[17] Xiong X, Song C L and Zhong Y L 1985 *Surface Physics* (Shenyang: Liaoning Science and Technology Publishing House) p. 76 (in Chinese)

[18] Hasegawa Y and Avouris Ph 1993 *Phys. Rev. Lett.* **71** 1071

[19] Garcia N and Serena A P 1995 *Surf. Sci.* **330** 665