Effect of rapid thermal processing on surface plasmon resonance of Ag island films

P. CHENG, D. LI[a,*], D. YANG[a]
[a]*School of Electronic and Information Engineering, Ningbo University of Technology, Ningbo, 315016, People's Republic of China*
[b]*State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*

The effect of rapid thermal processing (RTP) on surface plasmon (SP) oscillation characteristics of Ag island film are reported in this paper. With increase of the annealing temperature, the SP resonance band showed a blue-shift at first and red-shift finally which can be attributed to the morphology change of the Ag island films. The SP bands of large island size films blue-shift more in comparison with that of small islands due to their more obvious change of morphology upon annealing. By comparing the SP evolution of the Ag islands under RTP at different temperatures with those upon long-time furnace annealing (FA), it is found that the SP resonance band shifts directly to short wavelength by RTP, but the SP resonance band blue-shifts gradually with increasing the temperature by FA. The difference can be ascribed to the different heating and cooling rates between the two annealing processes.

(Received March 25, 2011; accepted April 11, 2011)

Keywords: Surface plasmon, Ag island films, Rapid thermal processing

1. Introduction

Interest in SP oscillation of noble-metal nanostructures has experienced explosive growth in recent years due to its applications in data storage, chemical and biological sensing or surface enhanced spectroscopy. At the same time, a lot of fundamental interest has been focused on the diverse metallic nanostructures preparation and their SP resonance tailoring [1-4]. Metal island films consisting of the metal particles deposited on a substrate represents one of the most basic cases of metallic nanostructures. They have the merits of relatively stable, low cost and easy to fabricate in large scale. Evaporation or sputtering is usually used to fabricate metal island films. It has been found that precise control of deposition parameters such as substrate temperature, deposition rates and film thickness allows the production of metal island films with tunable surface plasmon resonance wavelength [5-7].

Post-annealing was also used to tailor the morphology as well as the SP resonance of the metal island films. Many studies on metal island films after heating at varying temperature or in different atmosphere have been reported [8-11]. However, the furnace processing used in their experiment usually required a relatively long time. Rapid thermal processing (RTP), as a key reduced thermal budget process featuring high heating and high cooling rates, was also performed on metal films in several works, but most of the investigations were focused on the electrical properties [12, 13]. So far, there have been few reports delivering detailed investigation of the effects of RTP treatment on the SP resonant characteristics of Ag island films

In this paper, we present our findings on the morphology change as well as surface plasmon resonance evolution of Ag island films after RTP treatment. The experiment was carried out on Ag films with varying island sizes, and the heating temperature was varied from 200 °C to 500 °C. In addition, the SP resonance characteristics of Ag films under RTP were compared with the results under long time furnace thermal annealing.

2. Experimental

Ag island films were deposited onto 1 mm thick glass substrates by direct current magnetron sputtering of a 99.99% pure silver target at a working power of 60 W. Prior to deposition, the glass substrates were cleaned ultrasonically in ethanol for 5 min followed by in de-ionized water. The base pressure of the chamber was 5×10^{3} Pa. During the sputtering, argon gas with a flow rate of 30 sccm was introduced into the chamber and the growth pressure was maintained at ~10 Pa. The substrate temperature was held at 200 °C for *in situ* crystallization of Ag. The size of the Ag islands was controlled by sputtering times, and two series of samples with different sputtering times of 20 s, 45 s and 60 s were prepared.

Four different temperatures of 200 °C, 300 °C, 400 °C, and 500 °C were adopted in the thermal annealing for each series of Ag samples. RTP was performed in an Ar atmosphere for 60 s. Heating from room temperature to the highest temperature 500 °C was accomplished in 10 s, while cooling down to 60 °C required 30 s. FA was performed in the sputtering chamber which was first vacuumed under a pressure of $< 5\times10^{-3}$ Pa. The annealing time was 1 hour. The morphologies of the Ag island films were observed by a field emission scanning electron microscope (FE-SEM) (Hitachi S-4800). The absorption

spectra of the samples were carried out on an ultraviolet-visible absorption spectrophotometer (Hitachi U-1800).

3. Results and discussion

Fig. 1 (a), (b) and (c) show the SEM images of the as-prepared Ag films with sputtering time of 20 s, 45 s and 60 s respectively. It illustrates that at the sputtering time of 20 s, the film is composed of individual islands with a wide size distribution. With the increase of sputtering time Ag islands grow big gradually and finally grow into irregular grains at the sputtering time of 60 s. The mean diameters of the Ag particles are about 20 nm for the sputtering time of 20s, 60 nm for 45 s and 120 nm for 60s respectively.

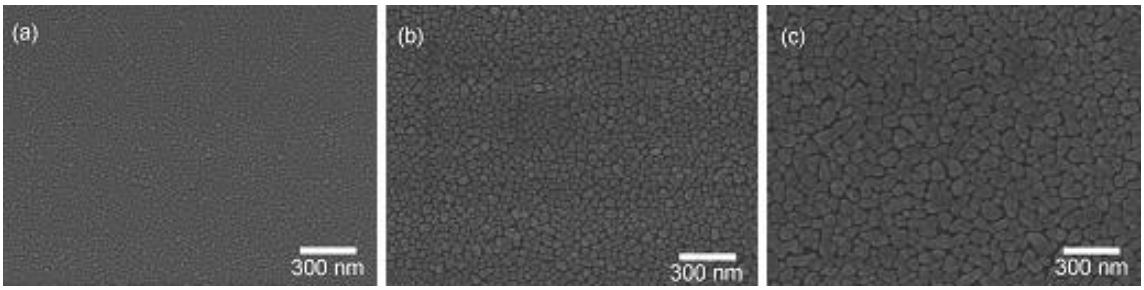

Fig. 1. SEM images of the Ag island films with different sputtering time (a) 20 s, (b) 45 s and (c) 60 s.

Fig. 2 (a)-(d) show the SEM images of Ag islands films with a sputtering time of 20s after RTP treatment at different temperatures ranging from 200 °C to 500 °C. Compared with the as-prepared Ag island films in Fig. 1 (a), the size distribution of Ag islands became uniform and the shape became more spherical. Moreover, with the increase of the annealing temperature, Ag islands contracted a bit and the vacancy between neighboring particles became wider. Similar change trends were also observed in the samples with sputtering time of 45 s and 60 s. SEM images of Ag island films with a sputtering time of 60 s after thermal treatment is presented in Fig. 3 (a)-(d). It can be found that the evident difference between the effects of RTP treatment on Ag islands with different sputtering time is the change of the Ag islands sizes. The diameters decrease after heat treatment but the change is slight for small size islands (sputtering time 20s), whereas RTP treatment causes a drastic change of size for big Ag islands (sputtering time of 60 s). The average diameter decreases sharply from 150 nm to about 80 nm after thermal treatment.

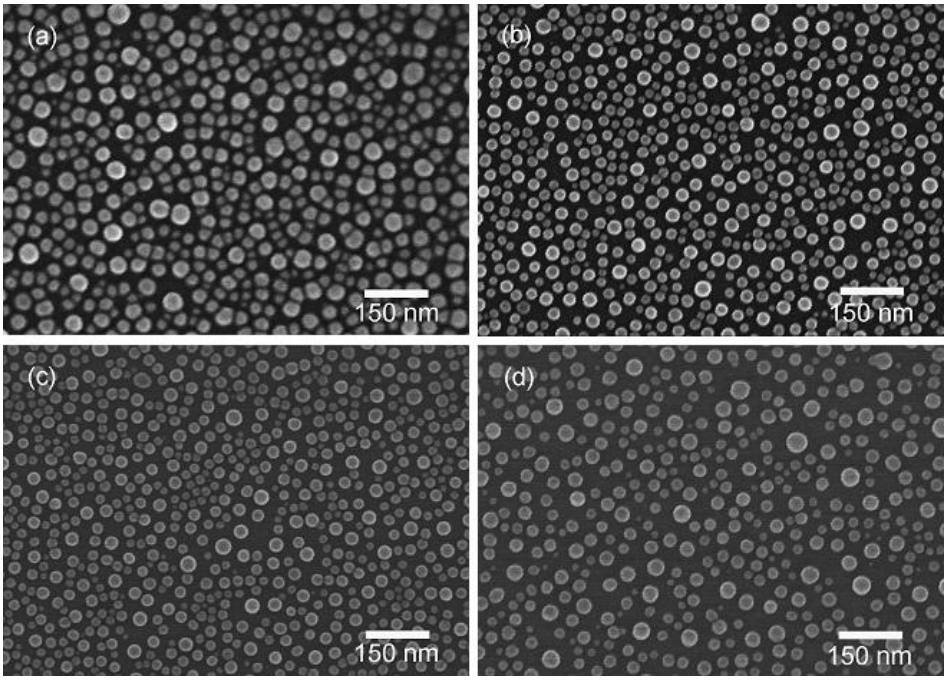

Fig. 2. SEM images of the Ag island films with a sputtering time of 20s after RTP at (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C.

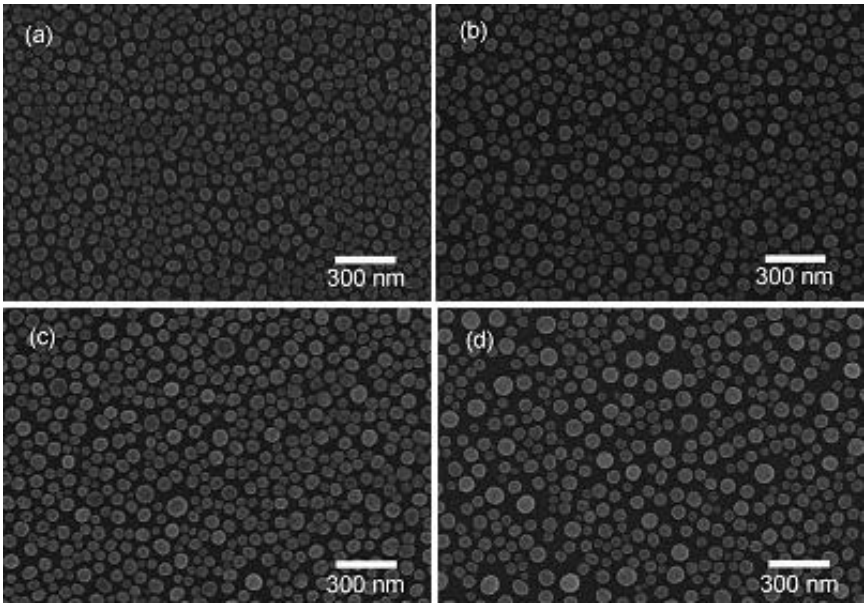

Fig. 3. SEM images of the Ag island films with a sputtering time of 60s after RTP at (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C.

Fig. 4 presents the absorption spectra of Ag island films before and after thermal annealing. (a) and (b) show the case of films with a sputtering time of 20 s and 60s respectively. Obviously, the spectra of all the samples are characterized by an absorption band related to the SP resonance. Two main effects are observed in the SP characteristics of all the samples: (i) blue-shift and narrowing of the SP resonance bands after thermal annealing. (ii) The SP resonance bands shift is sensitive to the annealing temperature.

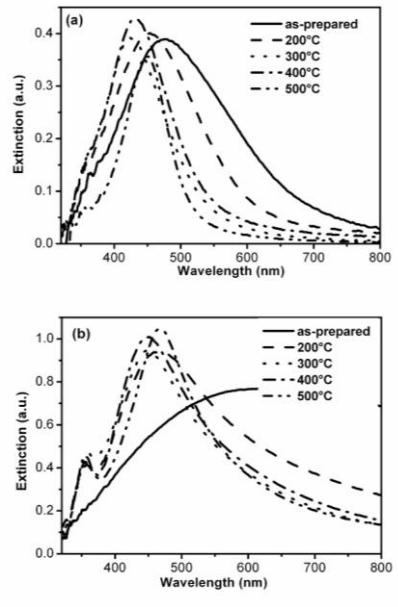

Fig. 4. Absorption spectra of Ag island films with a sputtering time of (a) 20s and (b) 60s before and after RTP.

To study precisely the effect of RTP temperature on the SP resonance, the evolutions of the resonance band position of all the samples were summarized in Fig. 5 (a). It can be seen that for as-prepared Ag island films with a sputtering time of 60 s, the LSP resonance band localized at about 590 nm. After annealing at 200 °C the LSP resonance band shifted sharply to 465 nm. With annealing temperature increasing to 300 °C, the resonance band blue-shifted further to 420 nm. However, the increase of annealing temperature to 400 °C and 500 °C did not cause the resonance band further blue-shift. The resonance band fixed near 460 nm at 400 °C and even red-shifted conversely upon annealing at 500 °C. Such resonance band evolution trends were also observed for samples with a sputtering time of 45 s and 20 s. But the band shift is slight for 20 s samples, the resonance band only changing from 475 nm to 420 nm after annealing at 400 °C.

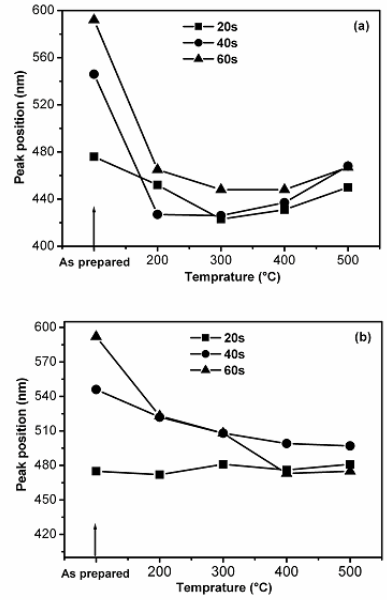

Fig. 5. Dependence of the SP band positions of the Ag island films on the thermal annealing temperatures (a) RTP, (b) FA.

The SP evolutions observed in Fig. 4 were in consistent with the morphology change of Ag island films observed in Fig. 2 and Fig. 3. As shown, before RTP the size of Ag islands is big and the shape is asymmetrical. Thus the LSP resonance band is broad which can be explained in terms of LSP multi-pole effects according to the Mie theory. After RTP at 200 °C, the Ag islands become smaller and more spherical, which causes the SP mode blue shift and band narrowing. The homogeneous size distribution also contributes to the SP resonance band narrowing. As the thermal treatment temperature increases to 300 °C, the high energy available to Ag atoms induces the Ag islands continue to contract, leading to the further blue shift of LSP resonance. Upon annealing at 400 °C, the Ag islands size does not change much, thus the LSP band is still near the position as that at 300 °C. However, annealing at a higher temperature of 500 °C causes the small particles around big particles fuse with big ones, leading to the Ag islands growing a little bigger and more separated. Accordingly the SP band red-shift slightly. One can see that RTP causes a substantial decrease in the size of big islands in comparison with that of small islands. Thus the SP resonance bands of 60s and 45 s samples blue-shift much more than that of 20s samples after RTP.

It is widely known that the morphology and optical properties of metal films can be change upon heating. Increasing of the particle size and a resultant red-shift of SP band was observed in some studies [10, 14]. The reason was ascribed to heating induced coalescence of small particles. However, surface strain during heating induced particle size decrease and blue-shift of SP resonance was also reported in literatures [15]. Our study demonstrates that annealing temperature in RTP decides the morphology changes and the resultant SP band shifts. In the range of T < 300 °C, the SP resonance peak blue-shifts with increasing annealing temperature. Above 400 °C, the SP resonance peak displays red-shift due to the coalescence of neighboring Ag islands.

FA were also done on the as-prepared samples to compare the difference between RTP and FA on LSP evolution. The experimental results were shown in Fig. 5 (b). As shown, for Ag island films with a sputtering time of 45 s and 60 s, the SP resonance band is dependent on the annealing temperature. The resonance bands also blue-shift with the increase of the temperature but the band shift trend is much gentler in comparison with that upon RTP. FA at 200 °C cause the SP band of the 45 s and 60s Ag films shift to about 525 nm. Whereas, after RTP treatment the SP peak shift to 425 nm and 470 nm for 45 s and 60 s films respectively. In particular, the SP band does not change for 20 s Ag films upon FA annealing but it blue-shift for RTP. All the results indicate that RTP has a different influence on the SP resonance of Ag island films in comparison with the case of FA.

The substrate and deposition condition of Ag island films used for RTP and FA are similar. So the difference in surface energy of samples is precluded. One possible difference between RTP and FA effect is the heating process. In RTP, the heating (cooling) rate and heat keeping time is short, so the change of the Ag island shape is completed in a short time, resulting in the SP resonance band shifting sharply to short wavelength. As the temperature is increased to high temperature up to 400 °C, Ag particles are provided high energy for coalescence and regrowth, leading to the formation of Ag islands with increased sizes and conversely red-shift of the SP band. In the case of FA, the SP band blue-shifting gradually with increasing of the temperature may be attributed to the Ag particles sufficient reshaping during long time heating process.

4. Conclusions

In summary, the change trends in particle structure and SP resonance peak of Ag island films as a function of increasing RTP annealing temperature was studied. The SP red-shift upon annealing at temperature < 300 °C due to particle size decreasing, and blue-shit as a result of size increasing as annealing temperature increased to above 400 °C. The results were found different from those of FA, which was attribute to the different heating process between RTP and FA.

References

[1] Jonathan J. Wierer, Jr, Aurelien David, Mischa M. Megens, Nature Photonics **3**, 163 (2009).
[2] Claire M. Cobley, Dean J. Campbell, Younan Xia, Adv. Matt. **20**, 748 (2008).
[3] Alexei A. Maradudin, Tamara A. Lekova, Physica B **405**, 2972 (2010).
[4] Kadir Aslan, Kerri McDonald, Michael J. R. Previte, Yongxia Zhang, ChrisD. Geddes, Chem. Phys. Letts. **464**, 216 (2008).
[5] M. Lončarić, J. Sancho-Parramon, M. Pavlović, H. Zorc, P. Dubček, A. Turković, S. Bernstorff, G. Jakopic, A. Haase, Vacuum, **84**, 188 (2010).
[6] Qu-Quan Wang, Jun-Bo Hun, Sha Ding, Gui-Guang Xiong, De-cheng Tian, Applied Surface Science, **243**, 329 (2005).
[7] W. A. Weimer, M. J. Dyer, Appl. Phys. Letts. **79**, 3164 (2001).
[8] Kuang-Che Lee, Su-Jien Lin, Chih-Hong Lin, Chih-Song Tsai, Yu-Jen Lu, Surface &Coatings Technology, **202**, 5339 (2008).
[9] P. Orfanides, T. F. Buchner, M.C. Buncick, Am. J. Phys. **68**, 936 (2000).
[10] L. V. Jing, Fachun Lai, Zhigao Huang, Yan Qu, Rongquan Gai, Proc. of SPIE, **6722**, 67222 (2007).
[11] R. P. Van Duyne, J. C. Hulteen, D. A. Treichel, J. Chem. Phys. **99**, 2101 (1993).
[12] Walter M. Kane, James P. Spratt, Lincoln W. Hershenger, J. Appl. Phys. **37**, 2085 (1966).
[13] C. W. Su, H. Y. Yo, Y. J. Chen, C. S. Shern, J. Appl. Phys. **97**, 124907 (2005).
[14] P. R. Gadkari, A. P. Warren, R. M. Todi, R. V. Petrova, K. R. Coffey, J. Vac. Sci. Technol. A **23**, 1125 (2005).
[15] R. Gupta, M. J. Dyer, W. A. Weimer, J. APPl. Phys. **92**, 5264 (2002).

* Corresponding author: mselds@zju.edu.cn