



## Stability of Ag nanoparticles fabricated by electron beam lithography

Wei Cao, Hani E. Elsayed-Ali\*

Applied Research Center, Old Dominion University, 12050 Jefferson Avenue, Newport News, VA 23606, USA

### ARTICLE INFO

**Article history:**

Received 18 June 2009

Accepted 22 July 2009

Available online 4 August 2009

**Keywords:**

Silver nanoparticles

Electron beam lithography

Stability

### ABSTRACT

The stability of silver nanoparticles on indium tin oxide coated glass substrates under atmospheric condition was investigated. These nanoparticles were fabricated using electron beam lithography. Energy dispersive spectroscopy analysis revealed a high concentration of sulfur in the silver nanoparticles exposed to laboratory air for 12 weeks at room temperature. Morphological changes in the silver nanoparticles were also observed for nanoparticles stored under the same conditions. In contrast, silver nanoparticles kept in vacuum did not show chemical or morphological changes after 12 weeks. The present work clearly shows the need to consider ambient exposure when using Ag nanoparticles for sensors.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Understanding the properties of Ag nanoparticles has drawn significant attention due to their potential applications in catalysis, photonics, electro-optics, and biological and chemical sensors [1–3]. Recently, fabrication of periodic Ag nanoparticle arrays for optical sensing applications utilizing their localized surface plasmon resonance (LSPR) properties has been extensively studied [2,4,5]. Among various processing techniques, electron beam lithography (EBL) is gradually becoming a widely used technique because it allows for fabricating nanoparticles with precisely controlled shape, size, and inter-particle spacing. To date, there have been numerous reports on the fabrication and optical properties of Ag nanoparticles. However, very little research has focused on the stability of EBL-fabricated Ag nanoparticles, which in turn determines the long term durability and reliability of biological and chemical sensors based on these nanoparticles.

The chemical degradation of silver, i.e. tarnishing and corrosion due to silver sulfidation, in ambient conditions has been widely known [6,7]. Early studies revealed that, under atmospheric conditions, silver forms a surface sulfide layer with low conductivity [6]. Hydrogen sulfide ( $H_2S$ ) was identified as a reactive agent for silver sulfidation. In a later study, Franey et al. [8] reported that carbonyl sulfide (OCS), commonly found in the atmosphere, can also readily sulfidize silver. Graedel et al. [7] further investigated the mechanism of silver sulfidation by  $H_2S$  and OCS, and the results indicated that higher relative humidity enhances the sulfidation processes for both species. Recently, McMahon et al. [9] reported significant red shift of the plasmon resonance peak on EBL-derived Ag nanoparticle arrays due to the formation of surface silver sulfide ( $Ag_2S$ ) layer over a short period

of time. Additionally, various research groups have also reported hillock and void formation in Ag thin films at elevated temperatures in different gaseous environments and on different types of substrates [10,11].

Clearly, the reliability of Ag nanoparticle based biological and chemical sensors is first and foremost contingent on the chemical and structural stability of Ag nanoparticles, especially in atmospheric conditions. In this paper, we report the chemical and morphological stability of Ag nanoparticles aged for 12 weeks at room temperature in laboratory air as well as in vacuum. The possible factors that may contribute to the chemical and morphological degradation of aged nanoparticles are also discussed.

### 2. Experimental

The Ag nanoparticles were fabricated using an ELPHY Quantum (Raith, Ronkonkoma, NY) EBL system attached to a scanning electron microscope (SEM, JSM-6060LV, JEOL, Japan). The substrates were microscope glass slides coated with 30 nm thick indium tin oxide (ITO) with resistivity of  $70\text{--}100 \Omega cm^{-2}$  (SPI Supplies, West Chester, PA). Each substrate was spin-coated with polymethyl methacrylate (PMMA) positive photoresist (MicroChem, Newton, MA), followed by electron beam exposure at 30 kV. Next, the sample was developed in a methyl isobutyl ketone (MIBK):isopropanol (IPA) developer (MicroChem, Newton, MA) with a ratio of 1:3 for 30 s, then rinsed in IPA for 30 s to stop the development. Ag thin films were then deposited on PMMA-patterned substrates using a thermal evaporation process with deposition rate of 0.5 Å/s to achieve film thickness of 40 nm. Finally, a standard lift-off process was carried out to obtain the nanoparticles with designed size and shape. Each nanoparticle array was designed to contain 225 Ag nanoparticles with inter-particle distance of 3.2 μm. To study the nanoparticle stability, some slides with fabricated Ag nanoparticle arrays were stored in vacuum ( $6 \times 10^{-2}$  Torr), while

\* Corresponding author. Applied Research Center, Old Dominion University, 12050 Jefferson Avenue Suite 721, Newport News, VA 23606, USA. Tel.: +1 757 269 5645; fax: +1 757 269 5644.

E-mail address: [helsayed@odu.edu](mailto:helsayed@odu.edu) (H.E. Elsayed-Ali).

others were stored in laboratory ambient conditions for various time intervals up to 12 weeks.

The surface morphology of Ag nanoparticles was characterized using scanning electron microscopy (SEM, JSM-6060LV, JEOL, Japan) and atomic force microscopy (AFM, Dimension 3100, Veeco, Santa Barbara, CA). The chemical analyses were carried out by energy dispersive spectroscopy (EDS, NORAN System SIX, Thermo Electron, Waltham, MA) attached to the SEM.

### 3. Results and discussion

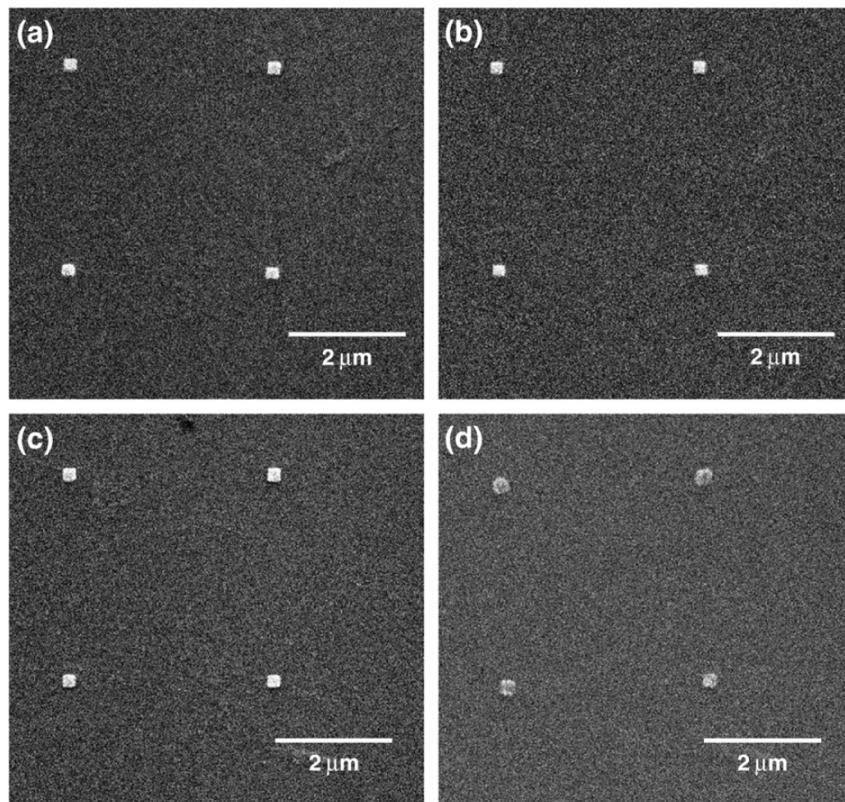
**Fig. 1(a)** and **(c)** shows SEM micrographs of as-fabricated Ag nanoparticles, while **Fig. 1(b)** and **(d)** shows SEM micrographs of the same particles after having been stored in vacuum and laboratory air, respectively, for 12 weeks at room temperature. It was observed that the nanoparticles stored in vacuum did not show noticeable changes in morphology, while the ones exposed to the atmosphere exhibited darkened surfaces and rounded edges. It should be noted that only portions of nanoparticle arrays are shown here to illustrate the morphology changes better, even though such changes were observed on the whole array. **Fig. 2** shows the EDS spectra obtained from two nanoparticles chosen from arrays shown in **Fig. 1(a)** and **(c)**, respectively. The results revealed the presence of sulfur on the nanoparticle exposed to laboratory ambient but not on the one stored in vacuum, which is also consistent with previously published results [9,12].

The chemical degradation of silver, i.e. tarnishing and corrosion due to silver sulfidation, in the atmosphere has been well studied. The process generally involves the formation of  $\text{Ag}_2\text{S}$  as a result of the chemical reaction between Ag and atmospheric  $\text{H}_2\text{S}$  or OCS [7,8]. Although previous research was mainly focused on Ag thin films, it is

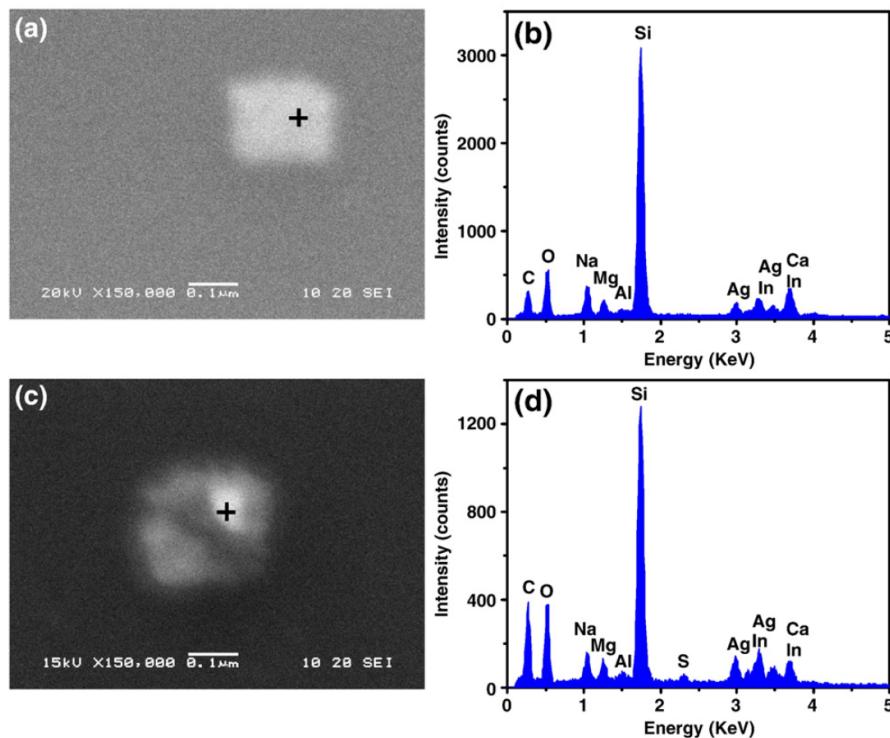
reasonable to assume that  $\text{Ag}_2\text{S}$  formation on Ag nanoparticles could occur at a higher rate due to their large surface-to-volume ratio. Indeed, the EDS quantitative analysis in the present work gives an atomic ratio between silver and sulfur of about 3.2 (close to the ratio of 2:1 for stoichiometric  $\text{Ag}_2\text{S}$ ), indicating a high sulfur concentration in the nanoparticle exposed to laboratory air for 12 weeks.

In addition to chemical degradation, the Ag nanoparticles on ITO-coated glass also exhibited morphological changes when exposed to laboratory air. As illustrated in **Fig. 1(d)**, square-shaped nanoparticles appeared to show rounded edges after 12 weeks in air. **Fig. 3** shows SEM micrographs of four square-shaped Ag nanoparticles exposed at room temperature to laboratory air for 1, 3, 7, and 12 weeks, respectively. It can be observed that the nanoparticle exposed to lab air for 7 weeks exhibited hillocks on the surface (**Fig. 3(c)**), while voids formed after 12-week exposure (**Fig. 3(d)**). Note that Ag nanoparticles from different arrays are presented in **Fig. 3**. This was done because we observed that electron irradiation at high SEM magnification caused Ag nanoparticles to breakdown into smaller particles quickly. Therefore, to minimize the electron irradiation effects, different nanoparticles were used for high magnification SEM imaging during the 12-week aging period. **Fig. 4(a)** and **(b)** shows AFM images of two triangular nanoparticles exposed in laboratory air for 1 week and 12 weeks, respectively. Nanoparticle height change can be clearly observed in **Fig. 4(b)**.

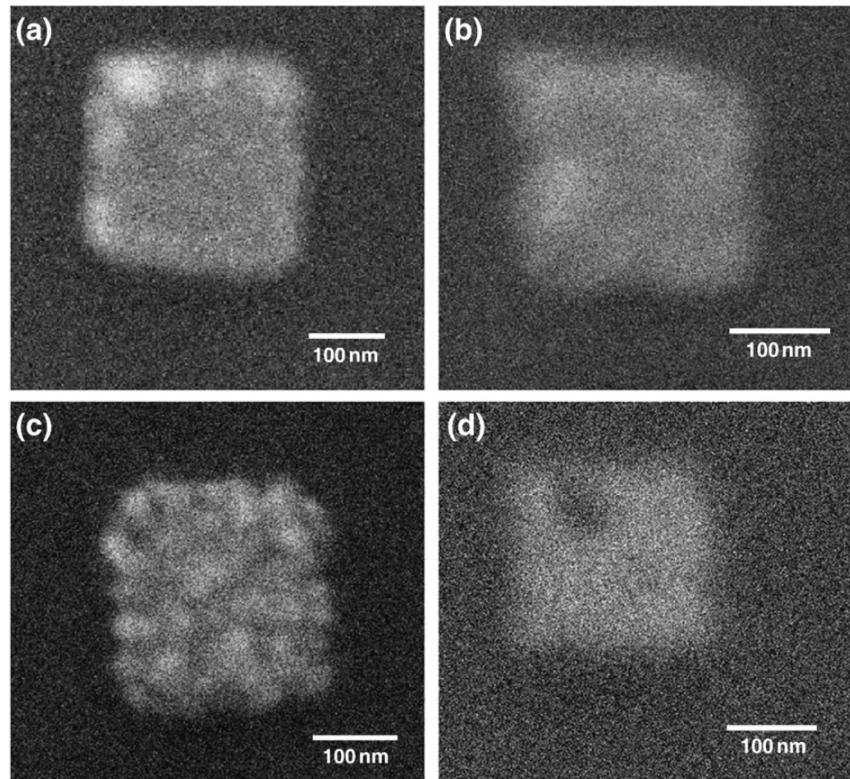
Although it is still unclear how the morphological changes on Ag nanoparticles occur, silver sulfidation could be an important factor since the nanoparticles stored in vacuum did not show noticeable morphological changes. It was reported that silver sulfidation does not occur uniformly on the silver surface, but rather forms a layer with the presence of randomly distributed clumps [6]. Elechiguerra et al. [12] also found that a thin layer of  $\text{Ag}_2\text{S}$  nanocrystals was formed on both



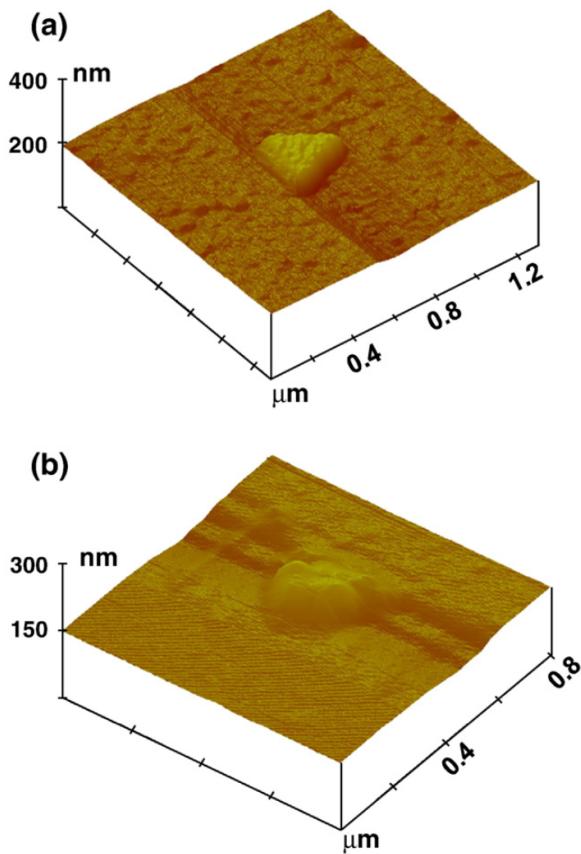
**Fig. 1.** SEM micrographs of (a) and (c) as-fabricated Ag nanoparticles, (b) Ag nanoparticles in (a) after storing in vacuum at room temperature for 12 weeks, and (d) Ag nanoparticles in (c) after being exposed to laboratory air for 12 weeks at room temperature.



**Fig. 2.** SEM micrographs and EDS spectra of Ag nanoparticles: (a) a single nanoparticle stored in vacuum for 12 weeks at room temperature; (b) EDS spectrum collected from the location marked in (a); (c) a single nanoparticle exposed to laboratory air for 12 weeks at room temperature; (d) EDS spectrum collected from the location marked in (c).



**Fig. 3.** SEM micrographs of Ag nanoparticles exposed to laboratory air for (a) 1 week, (b) 3 weeks, (c) 7 weeks, and (d) 12 weeks at room temperature.



**Fig. 4.** AFM images of two Ag nanoparticles: (a) 1 week after fabrication; (b) after exposure to laboratory air for 12 weeks at room temperature.

Ag nanowire and nanoparticle surfaces exposed to laboratory air for 5 weeks. Additionally, Ag nanowires with twin boundaries appeared to be more vulnerable to sulfur attack, some of which even completely decomposed to a number of crystals. In the present study, since Ag nanoparticles were obtained through lift-off processes from Ag thin films deposited by thermal evaporation, they generally resemble typical surface morphologies of polycrystalline thin films. Therefore, the combination of rough surfaces and defects, such as grain boundaries, could cause the nanoparticles to be easily attacked and corroded by the atmospheric sulfur [13].

The void formation in Ag thin films has also been studied by various research groups. Sharma and Spitz [14] reported a high density of small voids (15 Å) in Ag thin films deposited by sputtering after 8 weeks of aging at room temperature. They proposed that the void formation is mainly caused by the annihilation of excess vacancies due to significant vacancy diffusion at room temperature. In a successive study, Sharma and Spitz [10] annealed Ag thin films in different environments, including vacuum, oxygen, helium, and argon, at varying temperatures (215–470 °C) and observed hillock formation in all samples upon annealing. Moreover, annealing in oxygen resulted in void formation, and eventually island formation and agglomeration within the Ag films. Hence, they concluded that the presence of oxygen enhanced the surface diffusion of silver. Recently, Alford et al. [11] studied the stability of Ag thin films deposited on various substrates by electron-beam evaporation and annealed in vacuum at different temperatures. Their results indicated that the stability of Ag films is substrate dependent as voids formed at different annealing temperatures for different substrates.

Clearly, the void formation in Ag nanoparticles could be due to combined effects of multiple factors, besides silver sulfidation, such as defects, various diffusion processes, and stress conditions within the nanoparticles. The EBL-fabricated Ag nanoparticles generally possess high density of defects due to the nature of thin-film deposition techniques employed during the EBL process. When the nanoparticles are kept at room temperature for sufficient time, voids could readily form in the nanoparticles as a result of vacancy diffusion [14]. Furthermore, it has been reported that void formation and agglomeration can be affected by stress conditions within a film [15]. Although regular glass or ITO-coated glass have been mainly used as substrate materials for Ag nanoparticles fabricated for optical-based nanosensors, the literature data on microstructure of nanoparticles and interfacial properties of Ag/glass system are still lacking. The stress relaxation within Ag nanoparticles on glass could play an important role in void formation through grain boundary diffusion, interface diffusion, and surface diffusion of Ag atoms [16–18]. Additionally, since oxygen and water were found to enhance the silver sulfidation process [7,19], the atmospheric oxygen and high relative humidity may also contribute to the morphology degradation of Ag nanoparticles exposed to laboratory air.

#### 4. Conclusion

Silver nanoparticles fabricated on ITO-coated glass using EBL exhibited chemical and morphological instability in laboratory atmosphere at room temperature. The EDS results revealed significant amount of sulfur and SEM micrographs showed morphology change and void formation in Ag nanoparticles exposed to the laboratory air for 12 weeks. However, no sulfur was detected and no obvious morphology changes were observed on Ag nanoparticles stored in vacuum for the same period of time, indicating that Ag<sub>2</sub>S formation might greatly affect the morphology stability of Ag nanoparticles. The present experiment shows the need to consider Ag nanoparticle stability when using them for sensors.

#### Acknowledgements

This material is based on work supported by the National Science Foundation Grant No. NIRT BES 0507036.

#### References

- [1] Nallathambay PD, Lee KJ, Xu XHN. *Acad Nano* 2008;2:1371–80.
- [2] Zhao J, Zhang XY, Yonzon CR, Haes AJ, Van Duyne RP. *Nanomedicine* 2006;1:219–28.
- [3] Khanna VK. *Defence Sci J* 2008;58:608–16.
- [4] Barbillon G, Bijeon JL, Plain J, de la Chapelle ML, Adam PM, Royer P. *Surf Sci* 2007;601:5057–61.
- [5] Corrigan TD, Guo SH, Szmacinski H, Phaneuf RJ. *Appl Phys Lett* 2006;88.
- [6] Bennett HE, Peck RL, Burger DK, Bennett JM. *J Appl Phys* 1969;40:3351–60.
- [7] Graedel TE, Franey JP, Gaultieri GJ, Kammlott GW, Malm DL. *Corros Sci* 1985;25:1163–80.
- [8] Franey JP, Kammlott GW, Graedel TE. *Corros Sci* 1985;25:133–43.
- [9] McMahon M, Lopez R, Meyer HM, Feldman LC, Haglund RF. *Appl Phys B Lasers Opt* 2005;80:915–21.
- [10] Sharma SK, Spitz J. *Thin Solid Films* 1980;65:339–50.
- [11] Alford TL, Chen LH, Gadre KS. *Thin Solid Films* 2003;429:248–54.
- [12] Elechiguerra JL, Larios-Lopez L, Liu C, Garcia-Gutierrez D, Camacho-Bragado A, Yacaman MJ. *Chem Mater* 2005;17:6042–52.
- [13] Abbott WH. *IEEE Trans Parts Mater Packag* 1969;Pmp5:156–60.
- [14] Sharma SK, Spitz J. *Thin Solid Films* 1980;67:109–16.
- [15] Srolovitz DJ, Goldner MG. *JOM-J Miner Metals Mater Soc* 1995;47:31–6.
- [16] Coble RL. *J Appl Phys* 1963;34:1679–82.
- [17] Chaudhary P. *J Appl Phys* 1974;45:4339–46.
- [18] Presland AE, Price GL, Trimm DL. *Surf Sci* 1972;29:424–34.
- [19] Volpe L, Peterson PJ. *Corros Sci* 1989;29:1179–96.

