

Plasma-induced brightening and coarsening of tarnished Ag nanoparticles



Koichi Ozaki^a, Fumitaka Nishiyama^b, Katsumi Takahiro^{a,*}

^a Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan

^b Research Institute for Nanodevice and Bio Systems, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima, Hiroshima 739-8527, Japan

ARTICLE INFO

Article history:

Received 27 June 2015

Received in revised form

30 September 2015

Accepted 4 October 2015

Available online 8 October 2015

Keywords:

Ag nanoparticle

Localized surface plasmon resonance

Ar plasma exposure

Silver sulphide

Reduction of Ag₂S

Rutherford backscattering spectrometry

Particle induced X-ray emission

X-ray photoelectron spectroscopy

Mie theory

Atomic force microscope

ABSTRACT

The recovery of the optical properties of tarnished silver nanoparticles (Ag NPs) has been demonstrated using exposure to plasma. As-prepared Ag NPs on a SiO₂ substrate exhibited an intense localized surface plasmon resonance (LSPR) in the UV–vis optical extinction spectrum. The LSPR band weakened gradually when an Ag NP sample was stored in ambient air forming tarnished Ag. X-ray photoelectron spectroscopy (XPS) and ion-beam analysis revealed the presence of impurity elements, such as N and S. In addition, the shape of the valence-band XPS spectra changed significantly with exposure to ambient air. Ar plasma treatments recovered the intense LSPR and the XPS spectral shape. We conclude that both the reduction of Ag₂S to Ag and the morphological change toward isolated Ag NPs most likely lead to their recovery. A simulation based on the Mie theory, as well as direct observation with an atomic force microscope, supports our findings.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The optical properties of metal nanoparticles have been investigated experimentally and theoretically [1–4]. In particular, extensive studies have been reported for silver nanoparticles (Ag NPs) due to their attractive optical properties [5–7]. The localized surface plasmon resonance (LSPR) of Ag NPs is stronger than that of other noble metals. The intense LSPR band appearing in the UV–vis optical extinction is being used for many applications, such as chemical and biological sensors [8–12]. In addition, the Ag NPs exhibit a surface enhanced Raman scattering (SERS) effect [13–16], which is applicable to single molecule detection [17,18]. Ag NPs are, however, known to be rapidly tarnished, even in ambient air, as a result of the adsorption of extrinsic impurities, such as S and O [19–21].

McMahon et al. [21] measured the shift of the LSPR band for arrays of Ag NPs under ambient air conditions. These researchers revealed the presence of sulphur adsorbed onto Ag NPs determined

by Auger electron spectroscopy. The formation of an Ag₂S corrosion layer caused significant changes in the optical properties of the Ag NPs. As reported by Bennett et al. [19], a 0.1-nm-thick silver sulphide-tarnished film formed on evaporated Ag films stored in normal laboratory air after 1 h, and it increased to 0.3–0.6 nm after 1 day, 1.5–3 nm after 1 week, 6 nm or more after 1 month. Kuzuma et al. [22] investigated the LSPR band in self-assembled monolayers of Ag NPs experimentally, as well as through finite-difference time-domain (FDTD) simulations. The LSPR wavelength of the Ag NPs fabricated by chemical vapour deposition was measured to be ~440 nm, which is considerably greater than the calculated value. This discrepancy was explained by the formation of a core-shell Ag@Ag₂O structure.

In our previous study [23], XPS revealed the build-up of adsorbed impurities, including C, N and S, on the Ag NPs stored in our laboratory. Contamination of such impurities drastically weakens the LSPR band intensity, causing Ag NPs eventually to lose their capabilities for use in plasmonic applications. To maintain the plasmonic properties of Ag NPs, removal of the contaminated layer on the Ag NPs is necessary. Our study showed that the weakened LSPR recovered following low-energy Ar⁺ irradiation [23]. This recovery resulted from the removal of contaminants, including C, N and S

* Corresponding author.

E-mail address: takahiro@kit.ac.jp (K. Takahiro).

atoms. In addition, an earlier study by our group [24] showed that hydrocarbons adsorbed on Ag surfaces were eliminated effectively by Ar plasma exposure. During exposure, Ar plasma and/or energetic Ar ions remove contaminants on the Ag surface, resulting in a blue shift and a sharpening of the LSPR band in the UV–vis optical extinction spectrum.

In the present work, we examine the changes in the LSPR band of the tarnished Ag NPs upon exposure to Ar plasma. The relationship between the composition/morphology and optical properties of the Ag NPs exposed to Ar plasma are discussed, and finally, we show that the plasma treatment can be used to recover the intense LSPR band.

2. Experimental methods

Ag NPs were fabricated on synthetic silica (SiO_2) substrates and simultaneously deposited on highly oriented pyrolytic graphite (HOPG) for optical measurements and ion beam analysis, respectively. For the fabrication of Ag NP arrays, a desktop rotary-pumped sputter coater, SC-701 MkII, developed by Sanyu Electron, Co. Ltd., Japan was used with a silver plate sputtering target (purity: 99.8%). The pressure of the Ar gas was ~ 1 Pa, and the current was typically 8 mA at a voltage of 1.2 keV during the sputter deposition with a 30 s duration. The areal density of the Ag atoms was determined to be 1.6×10^{16} atoms/cm² using Rutherford backscattering spectrometry (RBS). Following the deposition, the samples of Ag NPs/ SiO_2 were aged in a vacuum ($< 7.0 \times 10^{-5}$ Pa) for 6 days prior to air exposure to stabilize the Ag NPs, e.g., morphology and crystalline structure. The samples were placed in ambient laboratory air for 46 days. The Ag/ SiO_2 and Ag/HOPG samples were subjected to the same conditions. The UV–vis extinction spectra were taken in standard transmission geometry in the wavelength range of 200–800 nm. A Mie calculation was performed using MQAggr 1.2 (Michael Quinten, Wissenschaftlich-technische Software).

For the Ag NPs/ SiO_2 samples placed in ambient laboratory air, X-ray photoelectron spectroscopy (XPS) using Mg K α radiation ($h\nu = 1253.6$ eV) was performed with a JEOL 9010 X-ray photoelectron spectrometer (JEOL, JAPAN). For the XPS measurement, the peak energy was calibrated using the Si 2p peak at 103.4 eV; Si is a constituent element of the substrate (SiO_2).

For the Ag NPs/HOPG samples placed in ambient laboratory air, Rutherford Backscattering Spectrometry (RBS) was conducted with 2 MeV-⁴He ions. Backscattered ⁴He ions were detected with a surface barrier detector placed at an angle of 165° with respect to an incident beam. Simultaneously, particle induced x-ray emission (PIXE) was employed with 2 MeV-⁴He ions. A Si (Li) detector with an appropriate filter made of polyethylene terephthalate was used to detect the characteristic X-rays generated from the target. Beams of ⁴He ions were produced from a single-end accelerator at Hiroshima University.

Plasma treatment with Ar was conducted using a Harrick Plasma PDC-32G operated at a power of 18 W. A large number of articles dealing with the application of this machine are listed on the home page of Harrick Plasma [25]. A chamber in the PDC-32G was evacuated to 0.8 Pa with a rotary pump. Ar gas was introduced to the chamber, keeping the pressure at 20 Pa during the plasma treatment.

A series of spectroscopic investigations, referred to as the first set of experiments, was followed by a second set of experiments based on microscopic observations to clarify the plasma-induced brightening mechanism deduced from the spectroscopic data. In the second set, the Ag/ SiO_2 sample was newly prepared under the same conditions as those used in the first set of experiments, and it was stored in ambient air for 35 days before observing its morphological changes with an atomic force microscope (AFM). During the

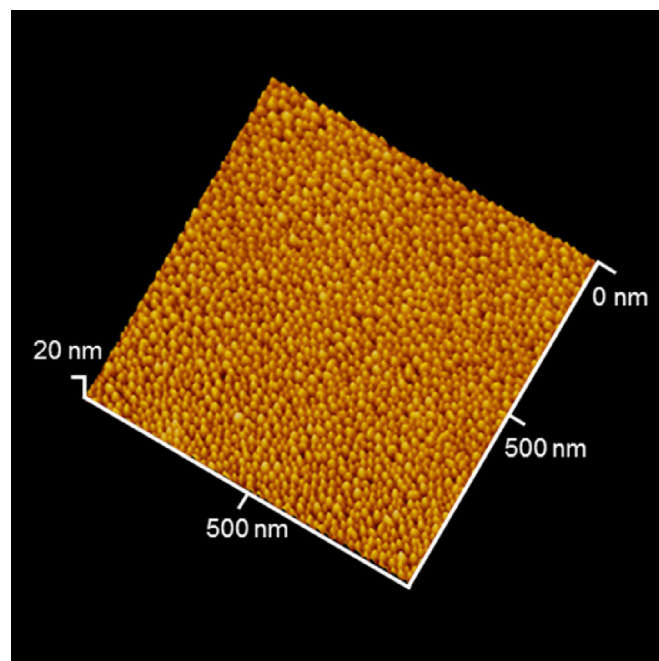


Fig. 1. An AFM image of as-prepared Ag/ SiO_2 sample that is aged in a vacuum for 6 days.

AFM observation, the dynamic contact mode (or tapping mode) of the Nanonavi Station manufactured by SII Nanotechnology, Japan was employed with a Si cantilever, SI-DF20S, with a tip radius of curvature that is less than 5 nm. For the as-prepared sample (aged in a vacuum for 6 days), Ag NPs with lateral sizes of 20–30 nm were observed with the AFM, as shown in Fig. 1.

3. Results

In the first set of experiments, we analyzed the spectroscopic data, including the optical extinction spectra, XPS spectra, RBS spectra and PIXE spectra, to discuss the compositional and morphological changes in Ag NPs induced by plasma exposure.

Fig. 2 shows the optical extinction spectra of the Ag/ SiO_2 in the wavelength range 200–800 nm. The Ag/ SiO_2 sample was aged in a vacuum for 6 days prior to air exposure. After placing in a vacuum, the LSPR band intensity and wavelength of Ag/ SiO_2 were 0.49 and 506 nm, respectively. The LSPR band located at 400–600 nm

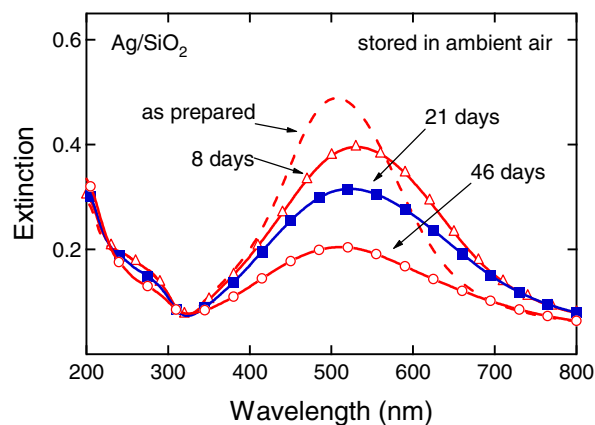


Fig. 2. The optical extinction spectra of Ag/ SiO_2 stored in ambient laboratory air at room temperature for 8 (open triangles), 21 (filled squares), and 46 days (open circles). The spectrum of the as-prepared sample (dashed lines) is also shown for comparison.

Download English Version:

<https://daneshyari.com/en/article/5356270>

Download Persian Version:

<https://daneshyari.com/article/5356270>

[Daneshyari.com](https://daneshyari.com)