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Growth of sputtered silver nanoparticles on a liquid mercaptan matrix with controlled viscosity and sputter rate

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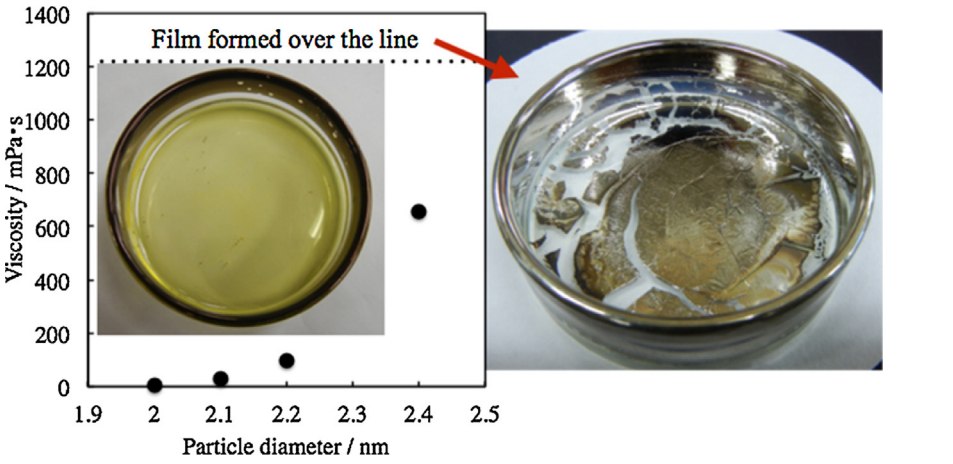
HIGHLIGHTS

- Silver nanoparticles were successfully prepared by matrix sputtering on a liquid matrix with four mercapto groups, PEMP.
- Growth mechanism of silver nanoparticles by sputtering on thiol organic matrix under the varied viscosities was investigated.
- Diameter of obtained Ag nanoparticles increased from 1.8 to 2.3 nm as the viscosity of the liquid matrix increased.
- Sputtering over mercaptan liquid matrix is a favorable method for the stable preparation of uniform very small nanoparticle of single nm order.

GRAPHICAL ABSTRACT



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ABSTRACT

A sputtering deposition of metals over liquid matrixes has been investigated as a novel and environmentally friendly method to generate stable colloidal metal nanoparticles. We have expanded this method by using the liquid monomers with mercapto groups in order to prepare more stable, uniform and size-controllable nanoparticles. Here we report the systematic investigation on the growth mechanism of silver nanoparticles on pentaerythritol tetrakis(3-mercaptopropionate) (PEMP) matrix under the varied viscosities controlled by temperature. The diameter of obtained nanoparticles increased from 1.8 to 2.3 nm as the viscosity of the liquid matrix increased, and at higher viscosity region we obtained a thin deposited film on the liquid surface but no nanoparticles formed. The effect of viscosity on the particle diameter was much smaller than previous works using ionic liquids or polyethylene glycol, and then the phenomenon was understood by the structure of these matrixes where PEMP has four mercapto groups however ionic liquids or polyethylene glycol does not have any functional groups that introduce strong interaction with metals. These demonstrations suggest that the sputtering over mercaptan liquid matrix is a more favorable method for the stable preparation of uniform very small nanoparticles.

1. Introduction

Sputtering is a well-established PVD process with a high degree of controllability in which atoms or clusters are ejected from a solid target material by bombarding it with energetic particles [1–3]. The

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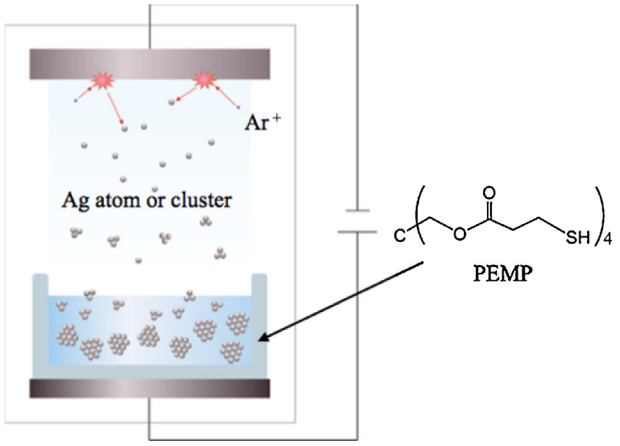

Fig. 1. Schematic illustration of matrix sputtering method and the chemical structure of PEMP.

high energy and controllable parameters of sputtering can result in the growth of well-structured crystalline films. Further, sputtering can be easily implemented for large-scale manufacturing and therefore, it has been widely used to prepare metal thin films.

Metal nanoparticles (NPs) or nanoclusters (NCs) have been extensively investigated due to their remarkable characteristics which make them highly promising for applications in catalysis, electronics, photonics etc [4,5]. Various preparation methods for uniform metal NPs have been developed; however, recently, metal sputtering over liquid matrixes has attracted a considerable attention to form stable colloidal metal NPs [6,7]. This method exploits the extremely low vapour pressure of liquid matrixes to deposit the NPs under high vacuum of the sputter chamber. Basically, ionized argon (Ar^+, generated by applying high voltage) attacks the target and ejects the target atoms or atom clusters into the vacuum chamber. Next, these species coalesce into NPs in the gas phase or at the interface of the liquid matrix (or aggregate further inside the liquid). Subsequently, non–volatile liquids such as ionic liquids, [7,8] liquid monomers [9–13] and polymers liquids [14,15] have been reported. This sputtering technique is promising as an environmentally friendly method for the synthesis of metal NPs due to of unnecessary reductants, whereas common chemical reduction methods generate harmful by-products and NPs with limited purity, especially due to the use of reductants. These investigations have enabled the synthesis of metal NPs (mostly Au NPs) with diameters in the range of 1–20 nm. Very recently, we reported a novel methodology to systematically control the diameter of resultant NPs on the order of a single nanometre by the introduction of mercapto ligands through two ways: the use of non–volatile mercaptans dissolved in the liquid matrix [11,15,16] or volatile mercaptans releasing gas molecules in the chamber [12]. We called these elaborate systems as *matrix sputtering method*.

Recently, the growth mechanism of metal NPs produced using a sputtering process has been investigated. It has been reported that the metal NPs mainly coalesce on the surface of the liquid matrix, [14,17] and then further coalesce and grow inside the liquid. This mechanism was revealed by controlling the viscosity of ionic liquids [17–19] or PEG [14], which affects the diffusion speed from the interface to the inside of the liquid matrix. A change in counter ion or temperature was attempted to control the viscosity of ionic liquids or PEG in previous works. Since these liquid matrixes have no functional groups that can introduce strong interaction with the surface of metal particles, the effect of viscosity was rather drastic resulting in wide particle size distribution from one nm (at lower viscosity) to several tens of nm (at higher viscosity).

To this end, we herein report a systematic investigation of the effect of the viscosity and the sputter rate on the particle size using the matrix sputtering method. The liquid mercaptan matrix, pentaerythritol tetrakis(3-mercaptopropionate) (PEMP, Fig. 1) was used and the viscosity was varied by changing the temperature. The effect of four mercapto groups of PEMP on the particle size is discussed and compared with the previous studies on ionic liquids and PEG.

2. Experimental section

2.1. Materials

Pentaerythritol tetrakis(3-mercaptopropionate) (PEMP, MW = 488.66, Aldrich) was used as the liquid matrix in the matrix sputtering synthesis. Water was purified using an Organo/ELGA Purelabo system (>18 MΩ cm). Ag target (99.99%) of 50 mmφ size was supplied by Tanaka Precious Metals (Tokyo).

2.2. Matrix sputtering synthesis of Ag NPs in PEMP

Specially designed magnetron sputter for matrix sputtering was used to prepare the Ag NPs. In order to remove gasses, water, and other volatile molecules from PEMP, it was first baked at 80 °C for 1 h under stirring at a reduced pressure with a rotary pump before use. We never observed any bubbles in the vacuum chamber during sputtering, which may affect the sputter rate and subsequent structures of the obtained NPs.

After being allowed to cool to room temperature, 7 g of PEMP was added into a 60 mmφ glass petri dish. Ag sputter deposition was carried out at a current of 50 mA under 2 Pa of Ar in the sputter coater. The experimental procedure is schematically illustrated in Fig. 1. A pressure of 2 Pa was selected because plasma formation during sputtering was not stable under very low pressure (such as 0.5 Pa). During the sputter deposition, the PEMP surface was positioned at a distance of 50 mm from the Ag target. Our unique sputtering system for NP preparation is equipped with a stainless stirring bar to stir the liquid matrix with high viscosity. The sputtering deposition was carried out for 20 min. The temperature of the sample stand was set to 0, 10, 20, 50, 70, and 100 °C, and the exact temperature was measured by using a chromel-alumel thermocou-

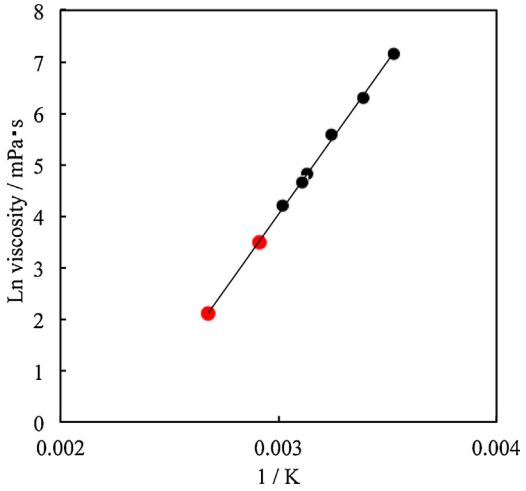

Fig. 2. The experimental viscosity (black circles) of PEMP as a function of absolute temperature and the corresponding fitting line. The red circles indicate the calculated viscosities at 70 and 100 °C using the fitting equation determined by the Andrade equation as described in the main text. The fitting equation: $y = 5940x - 13.78$, $R^2 = 0.999$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)