

Prevention of Coalescence Stage from Nuclei at Initial Growth of Thin Film by Substrate Rotation in Physical-Vapor Deposition

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ABSTRACT

Metal nanoparticles were fabricated on the powdery materials by a simple and unique method in which the kinetics of island growth at initial states of thin film in physical-vapor deposition (PVD) and the stirring of powders in a vessel were used. The stirring of powders in vacuum deposition prevented the metal islands from coalescing together and changing into thin film on the surfaces of powders, resulting in the formation of nanosized particles having the island size. The material properties of nanoparticles on the powders were characterized by various techniques and possible industrial applications were discussed.

Keywords: nanoparticles, powder, island, physical-vapor deposition, substrate rotation

1 INTRODUCTION

The study of nanosized particles has received considerable attention in the past few years due to their dramatic changes in the optical, electrical, and biochemical properties compared to bulk materials [1-4].

Various processing methods have been developed for the synthesis and commercial production of nanoparticles, including mechanical grinding, physical explosion in air or vacuum, and wet chemical processes using oxidation and

reduction reagents. Using the above conventional methods, however, it is difficult to make pure and uniformly size-distributed nanoparticles and to synthesize them from metal alloys, high melting metals, and ceramics [1].

In this study, we suggest a simple and unique method for synthesizing the nanoparticles attached to powdery materials by the conventional physical-vapor deposition (PVD). The formation mechanism of nanoparticles is also suggested on the basis of a thin-film-growth mode in vacuum deposition. The proposed method offers many advantages such as relatively simple apparatus, high-purity composition, uniform size distribution, and amenability to large-scale production.

2 EXPERIMENTAL

Synthesis of silver nanoparticles was carried out in a laboratory-type vacuum system equipped with a dc-magnetron sputter and a stirrer. Powdery materials were stirred in a stainless-steel vessel by a rotator whose speed was controlled by changing the ac voltage.

In order to observe the initial growth of Ag particles and to explain the difference in the size and shape of Ag particles prepared by static and dynamic modes, Cu grids were used as substrates. In the static mode, the substrates were located statically on the rotor of stirrer while facing the Ag target during the Ag deposition. They were also attached on the rotating rotor of stirrer in the dynamic mode,

where the Ag deposition was done periodically and discontinuously. If the time for one turn of the rotator is t , the Ag atoms were only deposited on the Cu grids during the active time, t_a , in which the Cu grids were exposed to the Ag target. During the inactive time t_i ($t-t_a$) in which the Cu grids were not exposed to the Ag target, the Ag deposition didn't occur. Time t could be varied by the control of the rotation speed of the rotor. For example, the t value was equal to 2 sec at the rotation speed of 30 rpm, at which the t_a and t_i were almost the same as 1 sec, respectively. The experimental equipments were described in detail elsewhere [5]. The material properties of nanoparticles were characterized by various analysis techniques.

3 RESULTS AND DISCUSSION

Figure 1 shows the photographs of the Ag-deposited Al_2O_3 powders with deposition time while rotating the rotor at 30 rpm. The color of the Al_2O_3 powders changes from the white of pure Al_2O_3 powder to yellow, and then to dark brown in 990 min. For comparison, the color of Ag thin films deposited on the PC substrate in the static mode changes from gray to bright metallic gray with the same deposition time. The yellowish color of the Ag-deposited Al_2O_3 powders may be attributed to a surface plasmon resonance by the formation of the nanosized Ag particles on the Al_2O_3 powders [6,7].

XPS analysis was performed to investigate the chemical states of the Ag deposited on the Al_2O_3 powders as a function of the deposition time while rotating the rotor at 30 rpm. As a reference, the 300-nm-thick Ag film on glass was deposited on the glass substrate. As shown in figure 2, the XPS $\text{Ag}3d$ peak area of the Ag deposited powders increases with deposition time, meaning the amount of the Ag deposited on the powder increased with deposition time. This trend is in good agreement with the results of

inductive coupling plasma (ICP) measurement (not shown here), in which the amount of Ag increases almost linearly with the increase of deposition time.



Figure 1: Optical images of pristine Al_2O_3 powder and Ag-deposited Al_2O_3 powders as a function of the deposition time; (a) pristine Al_2O_3 , (b) 150 min, (c) 390 min, (d) 550 min, (e) 770 min, and (f) 990 min.

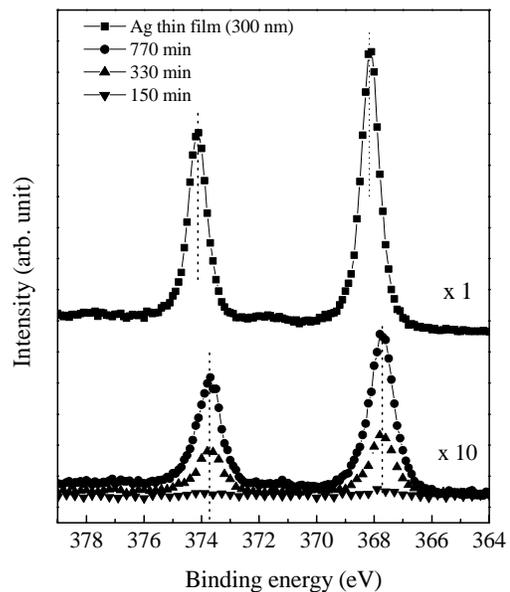


Figure 2: High-resolution XPS Ag 3d spectra of 300-nm-thick Ag thin film and Ag deposited Al_2O_3 powders as a function of the deposition time.

The binding energy of $3d_{5/2}$ peaks in the Ag particles deposited on the Al_2O_3 powders is fixed at 367.7 eV, which is lower than the 368.1 eV observed in Ag thin film. Although the amount of Ag deposited on the Al_2O_3 powders increases as a function of the deposition time, the peak positions and the difference in the binding energies between $3d_{5/2}$ and $3d_{3/2}$ aren't changed. From these results, it can be shown that the chemical states of Ag deposited on the powders is different from those of Ag thin film and are equal, irrespective of the deposition time and the amount of Ag. These XPS results agree well with the changes in the color of the Ag-deposited Al_2O_3 powders and show the Ag deposited on the Al_2O_3 powders is not a film shape, but nanosized particles.

The SEM pictures in figure 3 show the surfaces of Ag-deposited Al_2O_3 powders as a function of deposition time. No contaminants are detected on the bare Al_2O_3 powders, meaning that the powders have a clean surface. With deposition time being increased to 770 min (figure 3(b)), it can be seen that a number of Ag particles with uniform size distribution are formed on the surfaces. In order to identify the chemical composition of particles deposited on the surfaces, energy-dispersive x-ray spectroscopy (EDX) analysis was performed. Whereas only Al and O elements were detected in the area A of bare Al_2O_3 powders, the Ag element can be observed together with Al and O on the particle of area B, indicating this particle is pure silver.

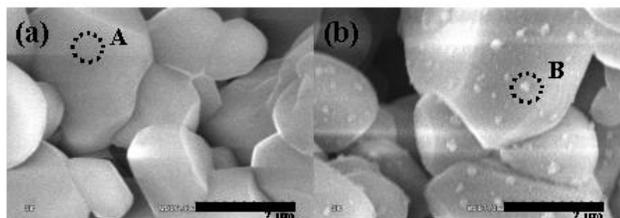


Figure 3: SEM micrographs of Al_2O_3 powder and Ag-deposited Al_2O_3 powders: (a) bare Al_2O_3 and (b) 770min.

To explain the formation mechanism of nanoparticles in our system, the deposition of Ag was carried out on the Cu grids attached on the rotator in the stirrer. Figure 4 shows the TEM images of Ag particles deposited on the Cu grids at same exposed time in the static and dynamic modes, respectively. In the case of static mode (figure 4(a)), the irregular Ag particles with a size distribution in the range of 1.0–25.0 nm are observed on the surfaces. Compared to the Ag particles deposited by the static mode, those prepared by the dynamic mode have a diameter less than 10.0 nm and uniform distribution. The number of Ag particles in a unit area also increased compared to those deposited by the static mode.

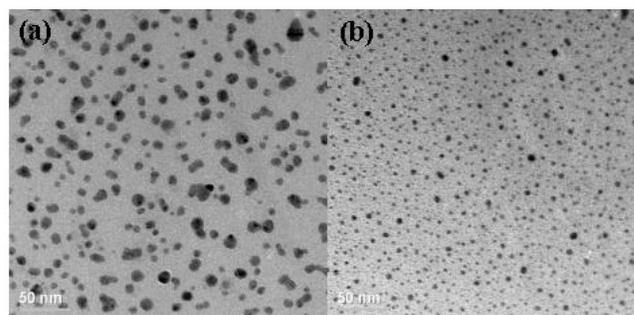


Figure 4: TEM micrographs of the Ag deposited on the Cu grids: (a) static mode and (b) dynamic mode.

In the mechanism of thin film growth, the nuclei are condensed or created on cooled substrates by the attachment of the vaporized atoms from a thermal or sputtering source, which is closely dependent on the change in Gibbs free energy (ΔG) [8]. An initial nucleus (a so-called embryo) would appear when ΔG becomes negative and then the embryo grows into the nuclei with decreasing the surface energy. Otherwise, the embryo would be re-evaporated into the vacuum or migrated to the neighboring nuclei in order to reduce the surface energy. As shown in the micrographs in figure 4(a) in which the Ag atoms are supplied continuously from the sputter source with

deposition time, the coalescence of islands happens subsequently with deposition time, with the result that large and irregular-sized islands are formed on the surface. In the case of the dynamic mode in figure 4(b), however, the supply of Ag atoms is interrupted during the inactive time in which the Cu grid no longer faces the Ag target and thus the continuous growth of islands and/or the coalescence of islands are also hindered. When the Cu grid faces the Ag target again, the depositing Ag atoms are changed into new nuclei on the surface, rather than being added to the existing islands. Through this procedure, the smaller and stable islands are easily formed on the surface, as shown in figure 4(b). It can be supposed that this phenomenon can be adapted to explain the formation of nanoparticles on the powdery materials in our experiment. When the Ag atoms are being deposited on the powdery materials which are being stirred continuously by rotor, the parts of the powder surfaces are exposed to the Ag target and the Ag atoms are supplied on the surfaces from the depositing source for the active time (t_a), which is similar to that in the above experiment using the Cu grids. But the supply of Ag atoms is interrupted instantly because powders are continuously stirred and the depositing surfaces don't face the Ag target anymore after t_a . If t_a isn't long enough for the continuous growth of islands and/or the coalescence of islands to happen on the surface of powder, the formation of nanosized and stable Ag particles can be expected, as shown in figure 4(b).

4 CONCLUSIONS

The nanoparticles having uniform size distribution were successfully prepared on the powders by using the conventional PVD method and stirring the powders. The amount of Ag on the powders increased as a function of deposition time, but the sizes and chemical states of the Ag nanoparticles remained constant irrespective of deposition

time. The growth mechanism of nanoparticles in our study was in good agreement with that of islands at initial stages of thin film growth in the conventional physical-vapor deposition. From this study, it is expected that our method can be a relevant way to synthesize pure metal, alloy, and ceramic nanoparticles on powders, which can be used as carrier having other functions.

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