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# Formation of Ag Aggregate on Glass Substrates using the Microwave Induction Heating

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The glycerol solution of $AgNO_3$ was irradiation by the microwave of 2.45GHz frequency from a commercial microwave oven. By the irradiation of microwave, the temperature of the reaction solution increased up to above the boiling point of glycerin. After ceasing irradiation, the color of the solution turned to yellow, and the fine silver particles were formed. From the XRD analysis, it was found that the resulting Ag fine particles are crystalline. It was shown that the glycerin efficiently reduced $AgNO_3$ to Ag in the microwave irradiation process. The sample after the irradiation showed the absorption in the visible wavelength region which originated from the plasmon excitation of Ag fine particle. From the laser scattering measurements, the Ag fine particles with the mean size of ～ 100nm were also found in the supernatant solution after the centrifugal separation. The SEM observations showed the formation of Ag aggregate of unequal size from 100nm to 500nm in the case of Ag plating on the glass substrate.

**Key words**: 2.45GHz microwave, Glycerol , $AgNO_3$, Microwave heating, Ag particle

## 1.INTRODUCTION

Microwave is the electromagnetic wave with frequencies from 300MHz to 300GHz ( in wavelength : 1 m ～ 0.1 cm ). The direct heating by using the microwave irradiation has features of uniformly heating for dielectric solutions or suspensions in short time. The origin of the heating is the direct interaction between microwave and a dipole moment and a dielectric polarization of the non-conductor. For example, the oxide ceramics with a large dielectric loss strongly absorbs the microwave.

Recently, it has been verified that the inorganic material synthesis is effective in the microwave irradiation field[1-4]. By irradiating ethylene glycol in which silver nitrate including poly(N-vinyl-2-pyrrolidone) dissolved as a surfacing chemical modifier with 2.45GHz microwave, Komarneni et al. reported that the silver particles of about 100nm size are formed, although any reducing agent does not coexist[5]. Because the dielectric constant of the glycerin is higher than that of ethylene glycol, the more efficient reaction by using the glycerol solution can be expected.

Based on the research of Komarneni et al., the preparation of Ag fine particles by the microwave irradiation for the glycerol solution of $AgNO_3$ with no surfacing chemical modifier was examined. In addition, an examination on the silver plating on glass substrates by microwave irradiation was also examined.

The aims of this study are to prepare a technology of the metal plating by the microwave irradiation to the little organic solution without emitting a waste water.

## 2. EXPERIMENTAL

The marketing reagent $AgNO_3$ (WAKO Co.,Ltd,>99.8%) was used as it is. The prime class glycerin (WAKO Co.,Ltd, >99.0%) was used for the solvent.

To begin with, a 100mM $AgNO_3$ aqueous solution was prepared. An $1cm^3$ of the $AgNO_3$ aqueous solution and $20cm^3$ of the glycerin were mixed and stirred. The concentration of finally obtained the glycerol solution of $AgNO_3$ is $5.0\times10^{-3}moldm^{-3}$. The solution was put into the cylindrical vessel made of the Pyrex with the cap above.

The microwave irradiation was carried out using a commercial microwave oven (TIGER Co.,Ltd; KRF-B 101:2.45 GHz 500 W) for 10 minutes. The sample temperature right after the heating was measured by an alumel chromel thermocouple.

The fine particle produced by the microwave irradiation were collected by the centrifugal separation (rotational speed; 6000rpm) for 5 minutes. The supernatant liquid was divided by the pipette, and the size distribution of silver fine particle was measured by the laser scatterometer (Ohtsuka Denshi, DLS-7000). The precipitate obtained by the centrifugal separation was dried under vacuum at room temperature for 1 week. Then, it was sufficiently washed by pure water. X-ray diffraction pattern of the dried samples were measured by using the Rigaku: RAD-II VC diffractmeter and CuKα radiation, and the crystal phases were identified.

The silver plating experiments were performed as follows. A $0.1cm^3$ of $AgNO_3$ grycerol solution was dropped on glass substrates by using a pipette. The concentration of silver nitrate in the dropped glycerol solution is $5.0\times10^{-3}moldm^{-3}$. The glass substrates were placed in a microwave oven for 10 minutes. The remained glycerol solution on the glass substrates after the microwave irradiation was washed out using pure water and it was dried under vacuum at room temperature for 1 day.

The formed silver aggregates strongly adsorbed on the glass substrates, and it did not detach during the cleaning process. Silver aggregate formed on the glass substrates was observed by a scanning electron microscope (JEOL; JNN-LA300).

## 3.RESULTS AND DISCUSSION

The solution showed the yellow color in 1 minute from the microwave irradiation start. The color change indicated the fine particle formation. Comparatively large fine particles were formed by the 10 minutes irradiation. The solution temperature right after the irradiation for 10 minutes was 180℃. Because boiling point of the glycerin was 154 ℃, the solution temperature rose higher than the boiling point at about 30℃ by the microwave irradiation. This seems to be "superheating effect" which originates for standing wave formed in the microwave irradiation field[6].

The X-ray diffraction pattern of fine particles obtained after the microwave irradiation for 10 minutes is shown

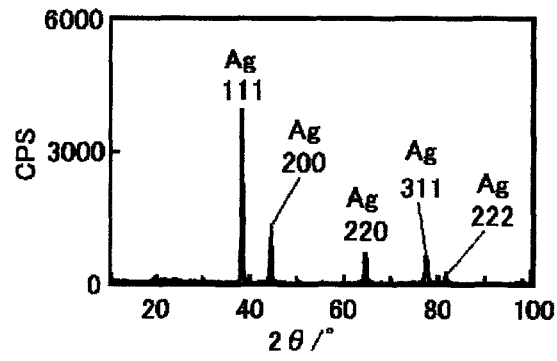


Fig.1 XRD pattern of the fine particles obtained after microwave irradiation for 10min to $5.0\times10^{-3}moldm^{-3}$ $AgNO_3$ · glycerol solution.

in **Fig.1**. The diffraction pattern shows clear peaks of fcc-Ag. The obtained fine particles were crystalline fcc-Ag[7]. Because Ag was formed under the conditions

in which a reducing agent does not coexist, it is suggested that the silver nitrate was reduced by the glycerin under the microwave heating process.

The absorption spectrum of supernatant solution obtained by the centrifugal separation of the sample after microwave irradiation is shown in **Fig.2**.

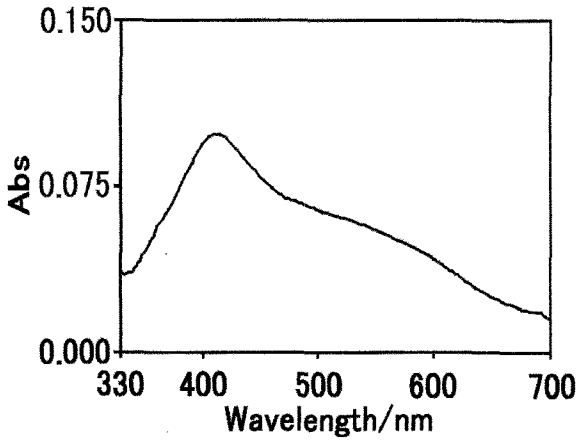


Fig.2 Absorption spectrum of supernatant glycerol solution after centrifugal separation.

The sample was diluted 20 times by adding glycerin. A comparatively sharp absorption peak near 410nm can be confirmed. Simultaneously, it can be confirmed that the wide absorption peak also exists in the vicinity of 550nm. These seem to originate from the plasmon absorption of the silver fine particles. It is reported that plasmon absorption of the silver fine particle strongly depends on the particle size[8], and the formed silver particles seem to have the wide distribution of size.

The distribution of the size of silver fine particles in the supernatant solution after the centrifugal separation were determined from the laser scattering measurement as shown in **Fig.3**.

The size of silver fine particles was widely distributed in the vicinity of 100nm. The wide size distribution agrees with the wide Plasmon absorption peaks in the visible wavelength region.

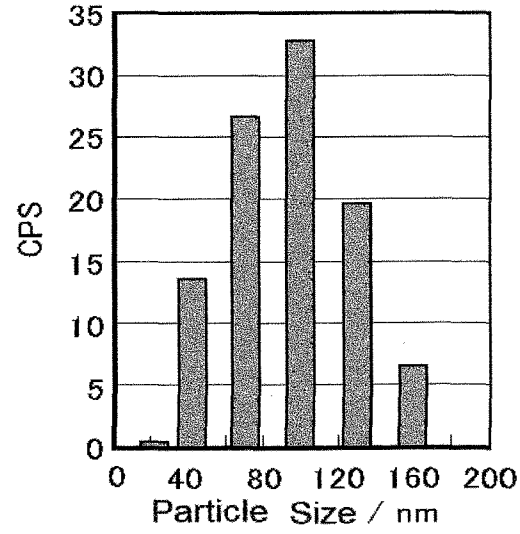


Fig.3 Size distribution of Ag fine particle in supernatant liquid after the centrifugal separation.

To examine the Ag plating, the microwave irradiation was carried out, after the glycerol solution of $AgNO_3$ was dropped on glass substrates. After the irradiation for 10 minutes, it was possible to confirm the formation of thin film of silver with the metallic luster on the glass substrates by microscope. In this experiment, a large amount of the glycerol solution evaporated during the irradiation process. A SEM image of the aggregate of silver fine particles formed on the glass substrates is shown in **Fig.4**.

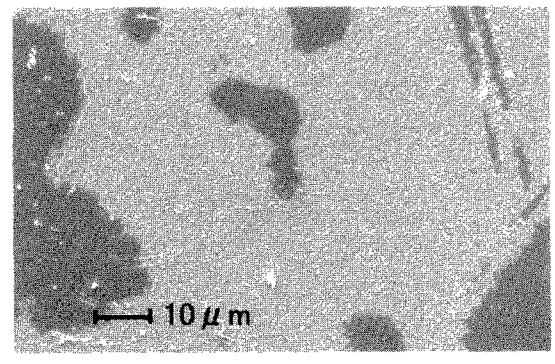


Fig.4 A SEM image of aggregate of the silver fine particles formed on the glass substrate.

The white part is covered by the aggregates of the

silver fine particles. The surface is considerably rough, and it is proven that it is not an aggregate of the minute silver particles. SEM image at higher magnification for the identical sample is shown in **Fig.5**.

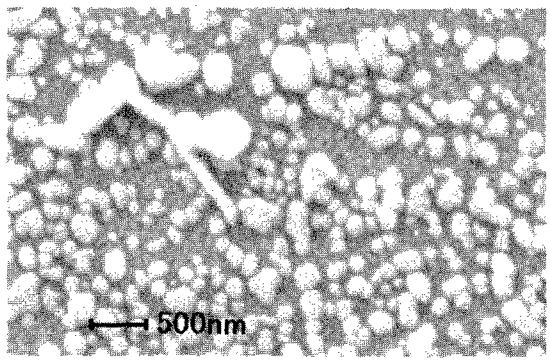


Fig.5 A SEM image of aggregate of the silver fine particle formed on glass substrates (A white part in Fig.4).

The silver aggregate in **Fig.4** is composed of fine particles with rather wide size distribution from 100nm to 500nm. The wider size distribution compared with **Fig.3** seems to originated from the evapotarion of the glycerol during the irradiation process. Under the same $AgNO_3$ concentration and volume of the dropped glycerol solution, the size distribution of silver aggregate formed on the glass substrates changed from 300nm to 800nm by lengthening a microwave irradiation time from 1min to 2min. This suggested that silver aggregate produced in the droplet glycerol solution with the evaporation process precipitated on the glass substrates.

## 4. CONCLUSIONS

Silver fine particle was formed by the 2.45GHz microwave irradiation for the glycerol solution of $AgNO_3$. Even if the surfacing chemical modifier did not coexist, the generation of the silver fine particle of about 100nm size was confirmed. The size of silver aggregate of silver fine particles formed on the glass substrates by microwave irradiation increased.

It is future problem to examine whether the formation of the minute silver aggregate under the coexistence of the surfacing chemical modifier is possible.

And, the pattern formation of the silver plating to the microscopic space region by the microwave irradiation can be expected with that the direct pattern description of a $AgNO_3$ glycerol solution on the substrate without the mask is enabled.

Because the recovery of the evaporated the glycerol solution by combining with the cooling system is possible, the construction of plating processing technology which does not discharge the waste water including the reuse of the glycerin is interesting.

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