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# Topological analysis for Au nanoparticles distributed in an Au/$SiO_2$ composite film by co-sputtering

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**Various Au/$SiO_2$ nanocomposite films were prepared by a co-sputtering method while controlling the number of Au wires, sputtering power, and sputtering time for the Au nanoparticulate monolayer films. The Au area fractions, Au mean particle sizes, and number densities for the Au nanoparticles of each Au/$SiO_2$ nanocomposite film were measured by image analysis of FE-SEM micrographs. Interparticle distances of Au nanoparticles were calculated using geometrical relationships.**

**Key words: Au nanoparticle, Au/$SiO_2$ nanocomposite, Co-sputtering, Topology, Interparticle distance, Image analysis.**

## Introduction

Extensive investigations have been carried out to physically or chemically fabricate Au nanoparticles because of their unique optical and catalytic functionalities. Most Au nanoparticles can be synthesized via various chemical methods including being homogeneously dispersed in the solutions as colloidal suspensions [1]. Also, various self-assembling techniques such as spreading a colloidal suspension on a solid substrate, field-enhanced or molecular-interaction-induced deposition from a colloidal suspension onto a solid substrate, and spreading a colloidal suspension of hydrophobic particles on a water surface and transferring it to a solid substrate allow the preparation of ordered and densely-packed nanoparticle arrays on solid surfaces [2]. However, it is difficult to produce Au nanoparticles having open surfaces without capping chemicals because most of the surface atoms in such Au nanoparticles should be stabilized by chemicals.

The co-sputtering method as a physical technique [3], in which two or more substances can be simultaneously deposited with long range uniformity is used to prepare Au nanoparticulate monolayered film with active surfaces. The sputtering method has been favorably applied to produce Au/$SiO_2$ nanocomposite films using various approaches including deposition of Au particles on a $SiO_2$ substrates [3], co-sputtering of Au and $SiO_2$ [4-7], and alternating sputtering [8-10]. As previously reported [11], the Au nanoparticles in Au/$SiO_2$ nanocomposite films produced by co-sputtering could be open to the outside with the chemical activity of a nanoparticulate monolayer film.

It is impossible, however, to obtain a well-ordered distribution of Au nanoparticles by co-sputtering although the Au nanoparticles can be very homogeneously deposited at long range. Therefore, a quantitative analysis of Au nanoparticles' topology is required to apply Au/$SiO_2$ nanocomposite films prepared by co-sputtering and to use the films for fundamental research. In this study, various Au/$SiO_2$ nanocomposite films were prepared as nanoparticulate monolayer films by a co-sputtering method and the interparticle distance of Au nanoparticles was evaluated in terms of number density, Au area fraction, and mean particle size of Au nanoparticles.

## Experimental Procedure

Au/$SiO_2$ nanocomposite films were prepared by radio frequency magnetron co-sputtering of Au and $SiO_2$ onto Si wafers. Au wires, 0.5 mm in diameter and 10 mm long, were set in a symmetric array on the $SiO_2$ target which had a diameter of 100 mm. The sputter deposition was performed under 0.53 Pa of Ar in a short time to obtain ultra-thin nanocomposite films. The preparation details are presented in table 1 along their notations. The morphologies of Au/$SiO_2$ nanocomposite films were observed by a field emission scanning electron microscope (FE-SEM). To calculate the Au particle size, Au area fraction, and interparticle distance, the FE-SEM micrographs were converted into perfect black and white images to distinguish Au nanoparticles. The ImageTool ver.2.01 Alpha 4 program was then employed for image analysis.

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**Table 1.** Fabrication details of Au/SiO$_2$ nanocomposite films and their notations.

| Notation | [a] | [b] | [c] | [d] | [e] |
|---|---|---|---|---|---|
| Number of Au wires | 48 | 48 | 48 | 24 | 84 |
| Sputtering power (W) | 10 | 25 | 50 | 50 | 50 |
| Sputtering time (minutes) | 60 | 5 | 1 | 2 | 1 |

## Results and Discussion

Fig. 1 presents various micrographs of Au/SiO$_2$ nanocomposite films deposited by co-sputtering. As indicated in table 1, the sputtering conditions were modulated to produce ultra thin films as a nanoparticulate monolayer and controlled to prepare similar particle sizes. Such films consisted of Au crystal nanoparticles (white dots) and an amorphous SiO$_2$ matrix (dark gray), as shown in Fig. 1. By molecular immobilization onto the surface of Au nanoparticles, exposure of Au nanoparticles to the outside was demonstrated, which was supported by the thinner thickness of the deposited SiO$_2$ compared to the Au particle size and by the interfacial characteristics between Au and SiO$_2$. The Au nanoparticles were homogeneously distributed over the entire substrates and they were mostly spherically shaped.

From the micrographs of each Au/SiO$_2$ nanocomposite film, the image analysis evaluated various topological details such as Au area fraction, Au mean particle size, and the number density of Au nanoparticles, as indicated in table 2. The Au area fraction, which indicates the two-dimensional coverage percentage of Au nanoparticles in the Au/SiO$_2$ nanocomposite film, mainly increased with the increase of the number of Au wires. Also, the number density of Au nanoparticles, which represents the number of particles in a unit area (1 μm × 1 μm), depended on the sputtering power when using the same number of Au wires. This was caused by sputtering yield and nucleation of Au nanoparticles. In our system, the sputtering yield was related to the sputtering power as $\frac{t_1}{t_2} \cong \left(\frac{w_1}{w_2}\right)^2$, in which $t$ is the thickness of the film and $w$ is the sputtering power. Therefore, a higher sputtering power could induce more nucleation of Au nanoparticles in the same period with interference of the growth of Au particles by the SiO$_2$ phase.

In a previous report [12], a topological analysis was performed for several Au/SiO$_2$ nanocomposite films with Voronoi diagrams. The interparticle distance was evaluated with the Au nanoparticle neighborhood defined

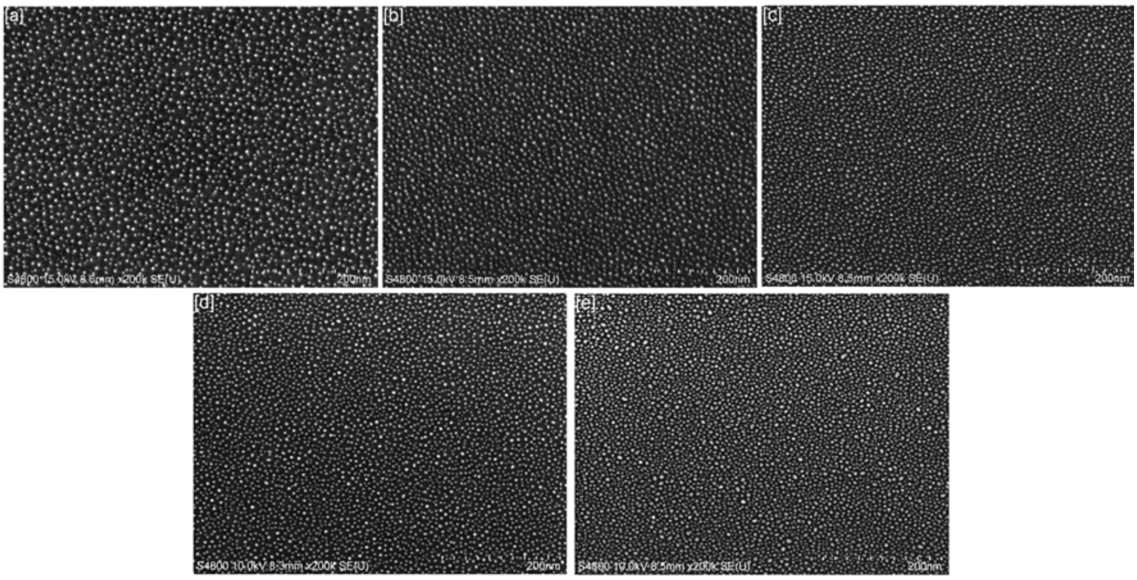


**Fig. 1.** Micrographs of Au/SiO$_2$ nanocomposite films produced using various sputtering conditions as indicated in Table 1.

**Table 2.** Image analysis results of Au nanoparticles in Au/SiO$_2$ nanocomposite films.

| Notation | [a] | [b] | [c] | [d] | [e] |
|---|---|---|---|---|---|
| Au area fraction (%) | 13.4 | 20.3 | 19.6 | 16.0 | 23.7 |
| Au mean particle size (nm) | 4.53 | 4.60 | 3.82 | 3.61 | 3.71 |
| Standard deviation of mean particle size | 1.19 | 1.48 | 1.04 | 0.96 | 1.19 |
| Number density (/μm$^2$) | 7,490 | 10,760 | 15,540 | 14,270 | 19,530 |

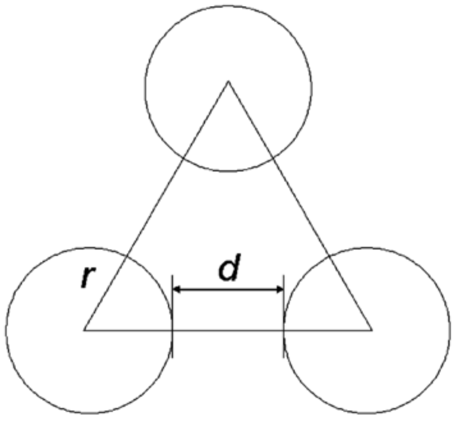


**Fig. 2.** Assumption of Au nanoparticle distribution.

by the Voronoi boundary in the Voronoi diagram [13, 14] resulting from micrographs of Au/$SiO_2$ nanocomposite films. On average, each Au nanoparticle had six neighbors. The interparticle distance between neighboring Au particles can be calculated with the assumption that Au particles are regularly distributed with hexagonal symmetry as for a (111) plane of a cubic structure as shown in Fig. 2. We approximated the interparticle distance ($a$) between the centers of Au nanoparticles using the area of the triangle of $\frac{\sqrt{3}}{4}a^2$ and $\frac{A}{N_\Delta}$ ($N_\Delta = 2N_{Au}$) as follows:

$$a = \sqrt{\frac{2A}{\sqrt{3}N_{Au}}},\ d = \sqrt{\frac{2A}{\sqrt{3}N_{Au}}} - 2r \qquad (1)$$

in which A is the total area of the analyzed image, $N_{Au}$ is the total number of the Au nanoparticles, $N_\Delta$ is the total number of triangles, and r is the radius of the Au nanoparticles. It is also necessary to introduce the Au area fraction, $A_{Au}^*$, in these relationships. The area fraction of Au can be defined as $A_{Au}^* = \frac{N_{Au}\pi r^2}{A}$ and it can be derived from Fig. 2 with Eq. 1 as $A_{Au}^* = \frac{2\pi r^2}{\sqrt{3}(2r+d)^2}$. Therefore, the interparticle distance can be related to the area fraction of Au as:

$$d = r\sqrt{\frac{2\pi}{\sqrt{3}A_{Au}^*}} - 2 \qquad (2)$$

By substituting Au particle size values of 1, 2, 5, and 10 nm in Eq. 1 and 2, Fig. 3 is obtained. As shown in Fig. 3a, the interparticle distance is approximately proportional to the number density with an exponent of –1/2. Also, at the same number density, the interparticle distance should decrease with increasing Au particle size. In this case, the area fraction should increase. With variations of the area fraction and the particle size of Au, changes of the interparticle distance can be expressed by Eq. 2 and as shown in Fig. 3b. The interparticle distance $d$ could be considerably decreased by increasing the area fraction and decreasing the Au particle diameter.

From table 2, the interparticle distances of Au nanoparticles for each Au/$SiO_2$ nanocomposite film could be calculated using the values of the Au mean particle

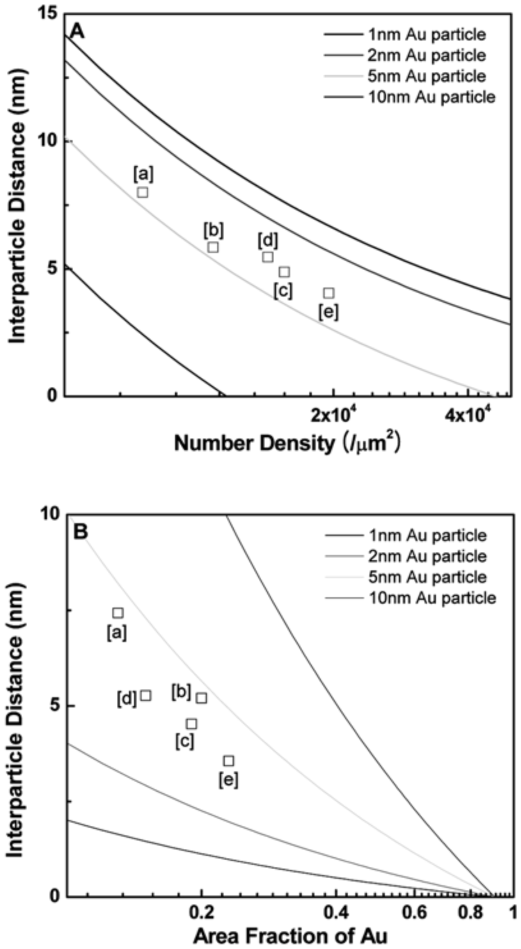


**Fig. 3.** Relationships between (a) the interparticle distance of Au nanoparticles and Au number density predicted by Eq. 1 and (b) the interparticle distance of Au nanoparticles and the Au area fraction calculated by Eq. 2 for various Au particle sizes. The interparticle distances of Au nanoparticles in various Au/$SiO_2$ nanocomposite films as shown in Fig. 1 are also shown in the graphs.

size, the number density, and the Au area fraction calculated by Eq. 1 and Eq. 2 as pointed out in Fig. 3a and 3b. The interparticle distance of the Au nanoparticles in Au/$SiO_2$ nanocomposite films decreased by increasing the number density at the same particle size (Fig. 3a). Also, the interparticle distance became smaller when increasing the Au area fraction in the Au/$SiO_2$ nanocomposite film as indicated in Fig. 3b. With the same number density, the interparticle distance decreased at larger particle sizes. In contrast, the interparticle distance decreased at smaller particle sizes with the same Au area fraction.

The topological analysis of nanoparticles distributed as a particulate monolayer film provides meaningful quantitative information for evaluating interparticle relationships. Such quantitative information about the relationships between nanoparticles will help to characterize their physical properties such as electric, optic, and/or magnetic properties as well as to predict possible applications of certain molecules for electrical connection between nanoparticles [11, 12].

## Conclusions

In the Au/SiO$_2$ nanocomposite films produced by co-sputtering, the Au area fraction increased with an increase of the number of Au wires and the number density of Au nanoparticles depended on the sputtering power when using the same number of Au wires. The interparticle distance of Au nanoparticles decreased by increasing the number density with the same particle size and by increasing the Au area fraction. With the same number density, the interparticle distance decreased at larger particle sizes. In contrast, the interparticle distance decreased at smaller particle sizes with the same Au area fraction.

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