Study of Thickness Distributions of Sputtered Gold Particles Deposited on a Perpendicular Section for Enhancement of 3D MetA-SIMS

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(Received 14 January 2015; Revised 6 October 2015; Accepted 10 February 2016; Published 19 March 2016)

We investigated the thickness distribution of gold particles sputtered by a focused ion beam (FIB) and deposited on a section perpendicular to the irradiated surface. The calculation results were analyzed from the viewpoint of three-dimensional metal-assisted secondary ion mass spectrometry (3D MetA-SIMS), a novel method that uses sputtered metal particles to enhance the signal yield of organic samples. The calculated distributions showed characteristic shapes of deposited gold, which had both a steep area and a flat area. The former area can be used for determination of sputtering feature, and the latter area can be used as the target area in which the sample section is located. The amount of particles on the target area was calculated to be within a reasonable range, implying that 3D MetA-SIMS can be realized with this simple and reasonable process. In summary, we established the foundation for enhancing the scope and effectiveness of 3D MetA-SIMS.

I. INTRODUCTION

In secondary ion mass spectrometry (SIMS), enhancement of signal yield from the target leads to a more sophisticated analysis. Three-dimensional metal-assisted SIMS (3D MetA-SIMS) is a novel 3D analysis method that intends to enhance the signal yields of organic samples by irradiating a gold plate set at the rear of a target sample [1]. This method adopts a unique processing technique called “shave-off”, which uses a lateral focused ion beam (FIB) and completely sputters the surface of the sample to create a slightly damaged new section parallel to the FIB [2]. In the shave-off processing, a flat cross section developed by the line scanning of the Ga⁺ FIB continuously moves from one edge of the sample to the other within one scanning frame. 3D MetA-SIMS aims to accumulate gold particles on every shave-off surface via “shave-off”, because the signal yield of the metal-covered (also called “metal-assisted” [3, 4]) sample is expected to be enhanced.

According to Prabhakaran et al., gold thickness for effective enhancement of yield is about 2–8 nm [5]. Hence, in order to achieve this thickness via sputtering of a gold plate, the irradiation time and the positional relation of the FIB, gold plate, and target section should be well regulated. In this paper, we present calculations of the distribution of deposited gold particles on the section perpendicular to the irradiated gold surface. In addition, we propose a methodology for determining the irradiation conditions to suitably conduct 3D MetA-SIMS.

It is said that the angular distribution of sputtered particles can be described as a function of the cosine of the emission angle [6]. With this assumption, here we derived a formula for the thickness distribution of the gold film on a shave-off surface under the given sputtering conditions (Fig. 1). Using the obtained distribution, the amount of gold particles on a given area of the sample was calculated, and the optimum sputtering conditions were determined.

II. EXPERIMENTAL

A. Calculations

The angular distribution of sputtered particles from the beam spot of an FIB perpendicular to the surface is commonly described as a power of the cosine of the emission angle $\theta$.

$$D(\theta) = \cos^n \theta. \quad (1)$$

Here, $n$ is a parameter that depends on the target and beam conditions, normally taken as around 1 [7]. From
(1), the distance distribution $f(x)$ (in Fig. 2) is derived as follows:

\[
\int f(x)dx = \int \cos^n \left( \frac{\pi}{2} - \theta \right) d\theta = \int \frac{x^n}{(x^2 + h^2)^{n/2 + 1}} dx,
\]

where $x$ is the distance from the irradiation plane and $h$ is the height of the irradiation spot. Because the FIB is scanned from 0 to $l_1$ parallel to the deposition surface, the sum of distributions along $x$ by FIB scanning, $F(x, l_1)$ (in Fig. 3) is given by

\[
F(x, l_1) = \int_0^{l_1} \frac{x^n}{\sqrt{h^2 + l_1^2(x^2 + h^2 + l_1^2)^{n/2 + 1}}} dl
= \int_0^{l_1} \frac{hx^n}{\sqrt{h^2 + l_1^2(x^2 + h^2 + l_1^2)^{n/2 + 1}}} dl,
\]

where $l_1$ is the length of scanning line. Consequently, the planar distribution on the deposition surface, $G(x, a)$ (in Fig. 4), is described as follows;

\[
G(x, a) = F(x, a) + F(x, l_1 - a)
= \int_0^{a} \frac{x^n}{\sqrt{h^2 + l_1^2(x^2 + h^2 + l_1^2)^{n/2 + 1}}} dl
+ \int_0^{l_1-a-x} \frac{hx^n}{\sqrt{h^2 + l_1^2(x^2 + h^2 + l_1^2)^{n/2 + 1}}} dl,
\]

This integral cannot be calculated analytically. Therefore, approximate calculations were performed for $n = 0.5, 1.0,$ and $2.0$, respectively, and the shapes of the thickness distribution were visualized by plotting graphs.

**B. Actual measurement**

To verify the validity of the calculation results, an actual demonstration was performed. A gold plate having a thickness of 200 µm was set on a flat Si substrate. The Ga$^+$ FIB was scanned on the gold side with a width ($l_1$) of 40 µm. The height of the scanned line from the surface ($h$) of Si was 10 µm and the processing time was 71 s. Further, the accelerating voltage of the FIB was 30 kV, with a sample current of 13 nA. A confocal laser scanning microscopy (CLSM) image of the gold deposited on the Si substrate was obtained using a 3D laser scanning microscope (VK-X250, KEYENCE; depth resolution, 0.5 nm).

**III. RESULTS AND DISCUSSIONS**

**A. Calculations**

Figure 5 shows the calculation results. The values of the parameters $h$ and $l_1$ are $h = 1$ and $l_1 = 4$, respectively. It can be seen that The $G(x, a)$ is practically independent of $a$ when $1/4 l_1 < a < 3/4 l_1$. On the other hand, the $x$-dependence of $G(x, a)$ is remarkable. A peak top is observed around $x = 1$ and its height decreases as $x$ increases. Further, When $x$ is sufficiently large, the slope of the height decreases. Thus, low $x$-dependence of the gold thickness can be ensured by selecting a proper range...
FIG. 5. Calculated shapes of $G(x,a)$ for $n = 0.5$, $n = 1$, and $n = 2$ (left) and the corresponding side views for an area $1/4 l_1 < a < 3/4 l_1$ (right).

Considering the $n$-dependence, it is found that the shape of the distribution becomes gentler as $n$ increases, but the difference in thickness is not significant. Assuming that the thickness of gold for effective enhancement is 2–8 nm, the $n$-dependence can be disregarded. When more precise regulation of gold thickness is required, $n$ is determined by some measurements. The distance $x$ of the peak top (equivalent to $x/h$) increases with $n$. Therefore, by obtaining the position of the peak top in actual measurement, in turn, the value of $n$ can be estimated (cf. Section III.B).

Next, we present the calculation of (i) the gold thickness on the target area and (ii) the optimum irradiation time. The ratio of particles deposited on the area $a_1$ to $a_2$, $x_1$ to $x_2$ to the total sputtered particles ($p$) is given by

$$p = \frac{\int_{x_1}^{x_2} \int_{a_1}^{a_2} G(a,x) \, da \, dx}{2\pi l_1 \times \int_{0}^{\pi/2} \cos^n \theta \, d\theta}.$$  

(5)

The average growth rate of the thickness $T$ (nm·s$^{-1}$) is given by

$$T = \frac{I \times M \times Y \times 10^{15}}{e \times \rho \times N_A \times S} \times p,$$  

(6)

where $I$ is the beam current (A), $M$ is the atomic mass (g/mol), $Y$ is the sputtering yield, $e$ is the elementary charge (C), $\rho$ is the density of gold (g·cm$^{-3}$), $N_A$ is the Avogadro constant, and $S$ is the area of the target section ($\mu$m$^2$).

For example, when $n = 1$, applying a distribution in the range of $3 < x < 5$ gives nearly uniform gold thickness (“nearly uniform” means that the thickness in the thickest point is not twice as thick as that in the thinnest point). When applying this range to sample with a section of $20 \mu$m$^2$, the gold plate should be $30 \mu$m away from the section, and scanning should be carried out $10 \mu$m above the section at a width of $40 \mu$m for the nearly uniform deposition.

In this case, $p$ is calculated as 2.46%. When $I = 1.0 \times 10^{-8}$ A and $Y = 14$, $T$ is calculated as 0.91 nm/s. Provided that desirable average thickness of gold is 8 nm, calculations show that 9 s of irradiation is sufficient to achieve the desirable average, and this amount of the time is within the appropriate irradiation time.

B. Actual measurement

Figure 6 shows CLSM images of the actual shape of the gold film deposited on the Si substrate. The shape is in good agreement with the calculation results presented above. Based on the distance of the peak top ($x/h = 1.5$), the estimated value of $n$ is 2. Figure 7 shows the side view of CLSM image superimposed with the graph of the calculation result. The graph obtained with $n = 2$ shows good agreement with the experimental image. Thus, the calculation formula that we derived above is valid. Moreover, the amount of gold particles deposited on an arbitrary section of a sample under similar experimental conditions can be numerically estimated via calculations with $n = 2$.

From (5) and (6), the average thickness of the deposited gold film for $0 < x/h < 1.5$ is estimated as $2 \times 10^2$ nm, which is larger than the actual experimental value ($1 \times 10^2$ nm). This difference is assumed to be due to the generation of a trench on the irradiated gold plate.
Prolonged FIB irradiation might generate a trench, and the amount of sputtered particles is less than the theoretical value owing to the redeposition in the trench. Such factors need to be considered when the irradiation time is long. However, in practice, the irradiation time will be shorter than that in this experiment; therefore, the redeposition loss will be less than 50% as long as the irradiation conditions are sufficiently milder than those for this measurement, such that they will not have a significant impact on the yield enhancement.

Based on these results, the optimum sputtering conditions for yield enhancement will be determined.

C. Improvement of irradiation condition

1. Reduction of trench generation

An effective approach for reducing trench generation due to prolonged irradiation is expansion of scanning area. The distribution in the case of irradiation of a rectangular area was investigated. Figure 8 shows the calculation results under two different conditions: line scanning and area scanning. The shapes of both distributions are nearly identical, which indicates that broadening the scanning area has no significant effect on gold thickness. Therefore, when prolonged irradiation is required, it will be useful to expand the scanning area in order to reduce trench generation.

2. Broadening of flat area

A broader flat distribution leads to efficient use of the sputtered gold. In addition to the distribution by the main irradiation, another distribution whose peak top is located closer to \( x = 0 \) than that of the main distribution will broaden the flat area. Figure 9 illustrates this approach. Two irradiations are combined for distribution: (i) normal scanning and (ii) additional scanning with 1/6
of the height and 1/16 of the duration of the normal scanning. Under the assumption that flatness is defined as 5% of the height difference, this auxiliary irradiation leads to a 30% expansion of the flat area, and the utilization rate of the sputtered gold becomes around twice as high as that the normal case. Thus, a combination of scanning processes effectively improves gold utilization.

IV. CONCLUSIONS

We proposed a methodology for determining the optimum sputtering conditions for 3D Meta-SIMS on the basis of some calculations. The validity of the calculation results was confirmed experimentally. We found that adequately short irradiation of a rear gold plate could produce sufficient gold thickness. Further, we presented some improved irradiation methods for more desirable film distribution. Thus, the scope and effectiveness of 3D Meta-SIMS can be enhanced on the basis of our results.

ACKNOWLEDGMENTS

The authors wish to extend their gratitude to Dr. Masato Morita from the Institute of Industrial Science for his skillful assistance in the experiments. We are also extremely grateful to Mr. Koji Kuramoto of KEYENCE Co. for his significant contribution in the CLSM measurement.