High-Yield Fabrication of Ag Films by Reel-to-Reel Pulsed Laser Deposition System

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Abstract. Ag films are deposited on REBCO tapes as a stabilizing layer by a sputtering method in the most case. The sputtering deposition has a disadvantage of material cost for wasted Ag due to a low deposition yield, contrary to the pulsed laser deposition (PLD) method. Therefore, we developed Reel-to-Reel PLD system to fabricate Ag films on tapes with the high deposition yield. As results, the PLD method has a deposition rate up to 1 nm/s as the sputtering method. The electrical resistivity of the Ag film by the PLD method is 4.7 times higher than the sputtering method. The deposition yield of the PLD method is 13 times higher than the sputtering method. Finally, the Ag film was deposited on moving tapes by using the developed Reel-to-Reel PLD system with a uniform thickness.

1. Introduction
The high temperature superconducting REBCO tapes consist of four layers such as a metal substrate, a buffering layer, a superconducting layer, and a stabilizing layer [1][2]. The stabilizing layer protects the superconducting layer from moisture and corrosion. Furthermore, the layer locally bypasses current and diffuses heat when dissipation appears in the superconducting layer. Bilayer of Ag and Cu are commonly used as the stabilizing layer of the REBCO tapes [3][4][5][6]. Ag is the optimum material for stabilizing layer because Ag has low electrical resistivity, high thermal conductivity [7], and is chemically stable with the REBCO layer. On the other hand, Cu is much cheaper than Ag and has modest properties as the stabilizing layer. However, it is fatal that Cu degrades REBCO when Cu is deposited directly on REBCO. Therefore, the combination of Ag and Cu is commonly chosen.

In most cases, the stabilization layer is fabricated by a sputtering method or e-beam evaporation [8][9][10]. The sputtering method has a large and uniform deposition area but has a disadvantage of a low deposition yield [11][12][13][14]. Due to the wasted material, the material cost increases when an expensive material such as Ag is used. On the other hand, the pulsed laser deposition (PLD) method has a small deposition area and a high deposition yield [15][16][17]. If the PLD method is adopted to fabricate the Ag stabilizing layer, a series of operations to fabricate the superconducting layer and the stabilizing layer can be performed by one apparatus since the superconducting layer is produced by
Reel-to-Reel PLD system [18][19][20]. In this study, we fabricated Ag thin films on metal tapes by Reel-to-Reel PLD system to improve the deposition yield compared with the sputtering method.

2. Experimental methods

We fabricated Ag thin films on Hastelloy© tapes and glass substrates with 10 mm width by the PLD method and the sputtering method.

First, the PLD method is described as follows. A KrF excimer laser Coherent, COMPex201 (wavelength: 248 nm), was used for the PLD method. The purity of Ag target used for the PLD is 99.98% (Nilaco). The deposition parameters were as follows: a laser energy of 90 mJ, a repetition frequency of 100 Hz, a back pressure of 10⁻³ Pa, a target diameter of 25 mm, a distance between target and substrate of 40-80 mm, a laser spot size of 1.8-2.2 mm², and an Ar pressure of 0-10 Pa. The distance between target and substrate was changed by adjusting the position of substrate holder, and the laser spot size was changed by adjusting the position of the focusing lens. First, Ag films were deposited on the fixed substrates to optimize the deposition condition. Then, an Ag film was deposited on a moving substrate to demonstrate uniform deposition on tapes.

As a comparison of the PLD method, a DC magnetron sputtering apparatus ACS-40000-C2 was used for a sputtering method. The purity of Ag target used for the sputtering is 99.99% (FURUYA METAL). In the method, Ag films were deposited on fixed substrates at a distance between the target and the substrate of 150 mm and at an electric power of 120 W. The target diameter of the sputtering method was 50 mm.

We analyze both the fabrication processes of the Ag films in terms of deposition rate, surface, crystalline, electrical properties, and yield. The thicknesses of the Ag films deposited by both methods were measured with an optical interferometry microscope Nikon, ECLIPSE LV150N. The deposition rate was calculated by dividing the film thickness by the deposition time. The surface of the Ag films on Hastelloy© tapes were observed using scanning electron microscope Hitachi High-Tech Science, S-3400N. The crystallinity of the Ag films on Hastelloy© tapes were analyzed using a multifunctional X-ray diffractometer Rigaku, ATX-G. The electric properties were measured by a four-probe method using Physical Property Measurement System Quantum Design, MODEL6000. In this measurement, the Ag films with a thickness of 2 μm on glass substrates instead of the Hastelloy© tapes were used to measure the accurate resistivity.

Finally, the yields of both the method was calculated from the weight gain of Ag deposited on the substrate and the weight loss of Ag target before and after deposition. The weight loss of the Ag target was measured using a balance METTLER TOLEDO, PB303-S. In the PLD method, the weight gain of Ag deposited on substrate was estimated by summarizing of the distributed thickness of Ag along a longitudinal direction and by assuming the typical density of Ag. At this time, the film thickness along the transversal direction was assumed to be uniform. In the sputtering method, the weight gain of Ag
film was estimated from the thickness of Ag films assuming that the uniform distribution of thickness throughout the deposition area of 78.5 cm$^2$.

3. Results and discussion
First, we discuss the experiments of the PLD method with the fixed substrate. Fig. 1 shows the distance between target and substrate dependence of deposition rate. The dotted line is a guide to the eye. The blue and the green lines assume the case for the ablated particle without and with the directivity, respectively. The blue line and the green line are based on the deposition rate at the distance between target and substrate of 20 mm. Both the lines are assumed that all particle fly directivity. However, the particle does not fly directivity and diffuse in the plane direction in reality, so these two lines do not match the experimental values. According to Fig. 1, the deposition rate was 0.028 nm/s and 0.445 nm/s when the distance between the target substrate was 80 mm and 20 mm, respectively. The deposition rate rapidly increased at the closer the distance. Theoretically, the density of the material evaporated from the target increases as decreasing the vertical distance from the target [15]. Therefore, the increasing at the deposition rate is due to vertical direction dependence of ablated Ag particle density. Ag particles evaporated from the target have directivity in the vertical direction, but some of the Ag particles diffuse in the plane direction since the plasma and the gas diffuse from a high pressure to a low pressure. Therefore, the particle density in the vertical direction decreases as going further away from target. The number of target particles deposited on the substrate and deposition rate decreases as increasing the distance between target and substrate. The particles diffuse in the vertical direction and there are few particles over an interface at which the pressure is sufficiently low, and plasma is transferred to the gas, so the deposition rate is about 0 and lower blue line. In Fig. 1, experimental values intersect with blue line at a distance between target and substrate of 80 mm. Fig. 2 shows the laser spot size dependence of deposition rate. As shown in Fig. 2, the deposition rate was 0.167 nm/s and 0.389 nm/s when the laser spot size was 1.8 mm$^2$ and 2.2 mm$^2$, respectively. The deposition rate increased for the larger laser spot size. In the PLD method, the plume shape change from spherical to linear as enlarging the laser spot size [15]. Therefore, the deposition area converges since becoming narrower the plume. The laser energy density decreases as enlarging the laser spot size since the laser energy is constant. As decreasing the laser energy density, the number of particles ablated from the target decreases and the particle energy also decreases. When it becomes lower than a certain energy, ablation disappears [21]. In our experiment, the target ablated even for the largest laser spot size. In Fig.2, the deposition rate depends mainly on plume shape since the deposition rate increases as enlarging the laser spot size. These results suggest that the smaller distance between target and substrate and the larger laser spot size increases the deposition rate of Ag in the PLD method. The deposition rate of PLD method is 3.67 times higher than that of the sputtering method since the deposition rate of sputtering method was 0.192 nm/s. For all the following results, Ag was deposited at the maximum deposition rate at distance between target of 20 mm and substrate and laser spot size of 1.8 mm$^2$. 


Fig. 1 Distance between target and substrate dependence of deposition rate of Ag film by PLD method.

Fig. 2 Laser spot size dependence of deposition rate of Ag film for the PLD method.

Fig. 3 is scanning electron microscope (SEM) images of Ag films deposited on Hastelloy substrates by using PLD and sputtering. In the PLD film, many droplets appear with sizes of 0.34-5.72 µm² and at the number density of 0.021 /µm². For the stabilizing layer, the size and the number density of the Ag droplets should be as small as possible because the overlapping of the droplets makes voids in the Ag layer which is fatal for the protection of the REBCO layer. As shown in Fig. 3, the number density times the size is 0.0071-0.12 smaller than 1. Therefore, the Ag layer is supposed to work as a stabilizing layer. The average surface roughness Ra was 2.44 nm and 1.89 nm in the PLD and the sputtered film, respectively. Since the droplets are large, Ra of the PLD film is about 1.3 times larger than that of the sputtering film.
We analyse a $\theta$-2$\theta$ x-ray diffraction pattern of the Ag films for both the methods. However, no diffraction peak was found. This result showed that these films consisted of amorphous phase of Ag.

Next, we deposited Ag film by the PLD method on the fixed Hastelloy substrates with different Ar pressure and with keeping all the other conditions same by aiming at the higher yield. Fig. 4 shows Ar pressure dependent thickness distribution of the Ag films. At Ar pressure of 5 Pa, largest thickness of 4.2 µm was obtained at the center of the films which is coaxially with the plume during the deposition. The distribution of film thickness is similar for the deposition condition at a back pressure and the Ar pressure of 10 Pa; the center of the film has a thickness of 2.5 µm. All the profiles have Gaussian-like distribution. FWHM of the central peak of the thickness is 24, 25, and 22 mm at the Ar pressure of ~ Pa, 5Pa, 10 Pa, respectively. During the Ag deposition at the higher Ar pressure, the ablated target particles converged near the center of the plume and the mean free path of the particles becomes short [22]. According to our results, Ar pressure of 5 Pa is the optimal condition for the high yield. When it is more than that, the yield decreases since the mean free path becomes shorter than the distance of 20 mm between target and substrate, and below that the yield decreases due to diffusion of target particles.
Fig. 5 shows Ar pressure dependence of the yield of Ag films. The yield of the Ag film with Ar pressure of 5 Pa is 31% and the highest.

Table 1 shows a comparison of the deposition parameters of the PLD method at the highest yield and the sputtering method. The resistivity for both the methods were shown in Tab. 1. As a result, the Ag film fabricated by the PLD has 4.7 times higher resistivity compared with than the sputtering film. The difference in the resistivity is considered to be due to droplets in the PLD film as shown in Fig. 3. The droplets make voids which disturb the current. Therefore, the electrical resistivity of the PLD film increases. To obtain the same performance as the stabilization layer of the Ag layer, the PLD method requires 4.7 times thicker Ag than the sputtering method. On the other hand, the yield of PLD method is about 13 times higher than the yield of sputtering method. Overall, the PLD method is 2.8 times more efficient than sputtering method. As a conclusion of the comparison for both the fabrication method of the Ag film, the PLD method is superior to the sputtering method in terms of material cost reduction.

![Fig. 5 Ar pressure dependence of the yield of Ag films.](image)

**Table 1 Deposition parameters of PLD and Sputtering.**

|                        | PLD          | Sputtering  |
|------------------------|--------------|-------------|
| Deposition time [min]  | 60           | 60          |
| Distance between target and substrate [mm] | 20           | 150         |
| Temperature [°C]       | 25           | 25          |
| Max thickness [µm]     | 4.2          | 0.9         |
| Target diameter [mm]   | 25           | 50          |
| Electrical resistivity [Ωm]     | $8.78 \times 10^{-8}$ | $1.86 \times 10^{-8}$ |
| Yield [%]              | 31           | 2.4         |
Next, we discuss the experiments of the PLD method with moving the substrate. Fig. 6 shows Ag film thickness distribution by moving PLD method using Reel-to-Reel system at tape speed of 0.36 m/h without Ar. The film thickness by moving system is controlled by tape speed. The stabilizing layer is deposited at one time with slow speed or deposited at many times with fast speed since Ag films do not change the properties when the films are laminated. In Fig. 6, the film thickness in the longitudinal direction was uniform as 300 nm. Therefore, it was suggested that the stabilizing layer of long tape is deposited by the Reel-to-Reel PLD system.

Fig. 6 Ag film thickness distribution by moving PLD method using Reel-to-Reel system.

4. Summary
We fabricated Ag thin films by the reel-to-reel PLD system to improve the deposition yield compared the sputtering method. The deposition rate of the PLD method increased by closing the distance between target and substrate and enlarging the laser spot size, and it is higher than sputtering method. The droplets in Ag were observed only in the films by the PLD method. The Ag films consisted of amorphous phase of Ag. In the PLD method, the yield of Ag was the highest at Ar pressure of 5 Pa, and it is about 13 times higher than that of the sputtering method. On the other hand, the resistivity of the PLD film is 4.7 times higher than that of the sputtering film. Overall, the PLD method is 2.8 times more efficient than the sputtering method in terms of material cost reduction. The uniform Ag film was deposited on moving tapes by using the Reel-to-Reel PLD system.

Acknowledgments
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