Effects of Irradiation Conditions of Laser Beam on Deposition Rate of LaNiO$_3$ Thin Films at Pulsed Laser Deposition

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To investigate effects of irradiation conditions of the laser beam on films prepared at the pulsed laser deposition (PLD) method, thin films of LaNiO$_3$ were prepared on quartz substrates under different irradiation conditions of the laser beam with the PLD method by using different lasers. The XeCl excimer laser or the Nd:YAG laser was used as a source of the laser beam. The spot size, the energy density and the energy of the laser beam at a target surface were changed as the irradiation conditions of the laser beam. The deposition rate and the surface morphologies of the films prepared on the substrates were estimated. As a result, it was found that the deposition rates of the prepared film with the XeCl excimer laser are determined by the spot size, and those with the Nd:YAG laser are determined by the energy of the laser beam. The surfaces of the films prepared by the XeCl excimer laser are smoother.

Keywords: pulsed laser deposition, deposition rate, irradiation condition, spot size, energy of laser beam

1. Introduction

The pulsed laser deposition (PLD) methods with various high-power lasers have been used for the thin film preparations of various materials such as oxides$^{1-7}$, nitrides$^{8,9}$ and so on. A clarification of a mechanism of the PLD has been tried by many researchers with various experiments$^{9,10}$ and computer simulations$^{9}$. However, the influence of laser kinds and the irradiation conditions of a laser beam on the film characteristics or the ablation phenomena have not been investigated in detail$^{11}$. If the influence is clarified, the film preparation according to the purpose is easier, and the computer simulations are more accurate.

In this research, we investigated the effects of the irradiation conditions of the laser beam on deposited films which prepared under different irradiation conditions of the laser beam with the PLD method by using different lasers. The XeCl excimer laser with the energy distribution of uniform intensity or the Nd:YAG laser (the third harmonics) with the energy distribution of Gaussian distribution was used as the laser beam source. The spot size, the energy density and the energy of the laser beam at a target surface of the laser beam were changed as the irradiation conditions of the laser beam. We choose a LaNiO$_3$ for the target material. The LaNiO$_3$ is metallic oxide with a perovskite structure. Therefore, we can easily estimate the characteristics of the deposited films, such as the deposition rate, surface morphologies, the electrical resistivity, crystallinity and so on.

Then we prepared the LaNiO$_3$ thin films on quartz substrates with the PLD method by using the XeCl excimer laser or the Nd:YAG laser. And the deposition rate and the surface morphologies of the prepared films on the substrates were mainly estimated.

2. PLD System and Experimental Method

Figure 1 shows the PLD system that was used for the thin film preparation in this research. The XeCl excimer laser (Lambda Physik, Lextra200, wavelength: 308nm, pulse width: 20ns) or the

![Fig. 1. Schematic diagram of PLD system](image-url)
Nd:YAG laser (Spectra-Physics, Quanta-ray Pro-250-30, wavelength 355nm [the third harmonics], pulse width: 6 - 9ns) was used as the laser beam source. A spherical chamber made from stainless steel (the inner diameter: 450mm) was used as a deposition chamber. The inside of the chamber was exhausted to a base pressure of 10^{-2} Pa by using a rotary pump (ULVAC, GLD-100) and a turbo molecular pump (Mitsubishi, PT-150-200H). And oxygen ambient pressure of 40Pa was enclosed.

A dense pellet of sintered LaNiO₃ was used as the target of the laser beam. To reduce the roughening of the target surface during the laser ablation, the scanning of the target surface with the focused laser beam was realized by rotation of the target by a motor. The spot size of the focused laser beam at the target surface was obtained by measurements of area of laser beam traces on a polaroid™ film which was exposed previously. The traces area on the polaroid™ film and the target surface are almost same in our laser irradiation conditions. The energy of the laser beam of the XeCl excimer laser was measured at the inside of the vacuum chamber with a joule meter (Gentec, ED-500) and a oscilloscope (Iwatsu, DS-6020). The energy of the laser beam of the Nd:YAG laser was measured at just front of the chamber with a power meter (OPHIR, 30AP-DIFF-SH). The energy density of the laser beam was calculated by dividing energy of the laser beam by the spot size.

Quartz glasses were used as substrates. Since the quartz glass is amorphous, the crystallinity of the substrate material does not affect for the crystallization of the deposited films. Substrate temperature was maintained at 450°C during the deposition. To reduce the crystallization of the deposited film by the substrate temperature, we used the relatively lower temperature than other researchers(1).

The distance between substrates and the target was 50mm. To make up the thickness of the prepared films to about 1µm, the deposition time was adjusted.

After the film deposition, the prepared films were cooled in oxygen of about 3kPa. The details of the experimental conditions, such as the spot size and the energy density of the laser beam and deposition time, were shown in Table 1.

The thickness and the surface roughness of the prepared films were measured by a surface roughness meter (Mitutoyo, SurfTest SV-400). The surface morphologies of the prepared films on the substrates were also observed by using an optical microscope (Keyence, VH-5000). We also measured the resistivities of the films by the four-probe measurements and the crystallinities of the films by the X-ray diffraction measurements. In this research, since repetition rates of the lasers are different depending on the laser kinds, the deposition rate of the LaNiO₃ film was expressed by the deposition quantity (height) per one-shot of the laser beam for comparison.

### Table 1. The deposition condition

<table>
<thead>
<tr>
<th>Laser</th>
<th>XeCl excimer laser</th>
<th>Nd:YAG laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>308</td>
<td>355</td>
</tr>
<tr>
<td>Spot size (cm²)</td>
<td>0.1 - 0.16</td>
<td>0.03 - 0.16</td>
</tr>
<tr>
<td>Energy density of laser beam (J/cm²)</td>
<td>0.7 - 1.5</td>
<td>0.8 - 3.6</td>
</tr>
<tr>
<td>Repetition rate of laser beam (Hz)</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>20 - 30</td>
<td>10 - 60</td>
</tr>
<tr>
<td>Target</td>
<td>Sintered LaNiO₃</td>
<td></td>
</tr>
<tr>
<td>Ambient gas pressure</td>
<td>40Pa (O₂)</td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>Quartz</td>
<td></td>
</tr>
</tbody>
</table>

### Fig. 2. The relations between the deposition rate and the spot size on the deposited films prepared by the XeCl excimer laser or the Nd:YAG laser

- (a) The case of the preparations with the XeCl excimer laser
- (b) The case of the preparations with the Nd:YAG laser

3.1 Effects of Spot Size on Deposition Rate Figure 2 shows the relations between the deposition rate and the spot size on the deposited films prepared by the XeCl excimer laser or the Nd:YAG laser. In the case of the films prepared by the XeCl excimer laser, Fig. 2 (a), it seems that the deposition rates are proportional to the spot size in the case of 1.0J/cm². Even by the
other energy densities, the deposition rates become similar values. Other hand, in the case of the films prepared by the Nd:YAG laser, Fig. 2 (b), the deposition rates of the prepared films become large as the spot size becomes large. As increasing the spot size of the laser beam, the ablated area become large and a quantity of substances emitted as the plume increases. Thus, the deposition rate of the prepared films increases.

However, when the energy of the laser beam of the Nd:YAG laser beyond about 0.1J/shot, the case of the spot size is larger than 0.1cm² with the energy density of 1.0J/cm², the deposition rate become dispersed with increasing the energy of the laser beam. In that case, large droplets are sometimes deposited on the films. This deposition of the large droplets causes the surface is rougher and the deposition rate is higher. And this irregular deposition of the large droplets causes the dispersion of the deposition rate.

3.2 Effects of Energy Density on Deposition Rate

The relations between the deposition rate and the energy density of the laser beam on the films prepared by the XeCl excimer laser or the Nd:YAG laser are shown in Figure 3.

Fig. 3 (a) shows the deposition rates of the films prepared by the XeCl excimer laser with the spot size of 0.14cm². The deposition rates are constant regardless of the energy density of the laser beam, except the case of 1.0J/cm². We considered that the deposition rates of the prepared films by the XeCl excimer laser are determined by the spot size of the laser beam because of the energy distribution of the laser beam of the XeCl excimer laser is uniform.

Fig. 3 (b) shows the deposition rates of the films prepared by the Nd:YAG laser with the spot size of 0.03cm². It seems that the deposition rates are proportional to the energy density of the laser beam. Since the deposition rates become large as the energy density of the laser beam become large even the same spot size, we deduced that the energy of the Nd:YAG laser beam has some contribution to the deposition rate. Then we investigated the effects of the energy of the laser beam of the Nd:YAG laser on the deposition rates in next subsection.

We need further study of the reason for the difference in the characteristics between Fig.3(a) and (b).

3.3 Effects of Energy on Deposition Rate

The relation between the deposition rates and the energy of the Nd:YAG laser beam on the prepared films is shown in Figure 4. It is found that the deposition rates are roughly proportional to the energy of the laser beam even the spot size was changed in the range of 0.03 - 0.16cm². Then we considered that the deposition rates are determined by the energy of the laser beam of the Nd:YAG laser.

Since the energy distribution of the laser beam of the Nd:YAG laser is Gaussian distribution, the energy at the central part of the laser beam is strong and there is a large quantity of photons. Therefore, the target tends to cause the multi-photon absorption. That is, as the energy of the laser beam becomes high, the quantity of photons at the central part of the laser beam increases regardless of spot size. This causes the multi-photon absorption at the target, and then the quantity of substances emitted as the
ablation plume increases. And it makes the deposition rate higher.

3.4 Effects of Laser Kinds on Surface Morphologies

The surface morphologies of the prepared films observed by the microscope are shown in Figure 5. The film, shown in Fig. 5 (a), was prepared by the XeCl excimer laser with the spot size of 0.13cm² and the energy density of 1.0J/cm². And the film, shown in Fig. 5 (b), was prepared by the Nd:YAG laser with the spot size of 0.13cm² and the energy density of 1.0J/cm².

In the case of the film prepared by the XeCl excimer laser, as shown in Fig. 5 (a), the size of droplets are small (submicron grade) and the number is comparatively few. The surface of the film is very flat. Other hand, in the case of the film prepared by the Nd:YAG laser, as shown in Fig. 5 (b), the size of droplets is slightly bigger and there are many droplets. Furthermore, a lot of unevenness is seen on the film surface. From the observations of the surface morphologies, it was found that the surfaces of the films prepared by the XeCl excimer laser are smoother than the films prepared by the Nd:YAG laser.

Figure 6 shows the surface morphology of the other film prepared by the Nd:YAG laser with the spot size of 0.04cm² and the energy density of 2.0J/cm². Fig. 5 (b) and Fig. 6 are typical examples of the irregular deposition of the large droplets that mentioned in 3.1. In the case of Fig. 5 (b), the large droplets are relatively few even the energy of the laser beam is 0.13J/shot. Other hand in the case of Fig. 6, the large droplets are many even the energy of the laser beam is 0.08J/shot. We need further study of the irregular generation and deposition of the large droplets.

The films shown in Fig. 5 (a) and Fig. 6 have lowest resistivity among the films prepared by each laser. The resistivities of the LaNiO₃ films shown in Fig. 5 (a) and Fig. 6 are \( \rho = 0.5 \ \Omega \cdot \text{cm} \) and \( \rho = 2.7 \ \Omega \cdot \text{cm} \), respectively. The films prepared by the XeCl excimer laser show lower resistivity than the films prepared by the Nd:YAG laser. It was found that the laser kinds also affect the resistivity of the prepared films.

The values of the resistivity of the films prepared in this study are relatively higher than those obtained by other researchers. This is because of the film preparations were done at lower substrate temperature of 450°C. From the X-ray diffraction measurements, it is found that the films prepared in this study are amorphous. This is why our films show the higher resistivity.

4. Conclusions

We investigated the effects of the irradiation conditions of the laser beam and the laser kinds on the deposited films. As a result, it was found that the factors determining the deposition rates change depending on the laser kinds. The deposition rates of the films prepared by the XeCl excimer laser are determined by the spot size, and those by the Nd:YAG laser are determined by the energy of the laser beam. The surfaces of the films prepared by using the XeCl excimer laser are smoother.

Usually, in the computer simulation of the laser ablation, the energy density of the laser beam and the irradiation time are taken into consideration as factors of the laser beam. However, it was found from present research that the energy value and the energy distribution of the laser beam should be also considered in the computer simulation of the laser ablation with the Nd:YAG laser.

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References


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