Size distribution of droplets in film prepared by pulsed laser ablation

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Abstract

Volume and size distribution of droplets in oxide films were investigated for a variety of laser fluences, wavelengths and target temperatures. Effects of both the ambient gas pressure and the substrate temperature on the droplet formation was investigated. It was found that the increase in the ratio of the droplet volume to the film volume V_d / V_f caused by increasing the maximum etching depth of target per laser shot d_e ($V_d / V_f \propto d_e^{\,3}$,as previously reported) due to changes in the deposition conditions other than the target temperature is mainly attributed to an increase in the formation of large droplets. It was also found that the correlation $V_d / V_f \propto d_e^{\,3}$ is valid also for elevated target-temperatures, and the increase in the target temperature enhances the formation of small droplets compared with large ones. The effect of cooling of droplets after the ejection from the target due to the ambient pressure and/or the substrate temperature is discussed.

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1. Introduction

Formation of droplets in oxide films prepared by pulsed-laser-ablation (PLA) deposition is still an obstacle to be overcome. It is important to investigate the mechanism of droplet formation in order to study the laser ablation phenomenon and to reduce droplets in the films. So far many papers have reported a positive correlation between the amount of droplets and various parameters such as the target porosity[1], the deposition rate[2], the laser fluence[3], and the wavelength[4,5]. We also have already reported that the ratio of the droplet volume to the film volume (V_d / V_f) is proportional to $d_e{}^3$ (d_e being the maximum etching depth of the target per laser shot) for a variety of ablated materials and laser wavelengths using substrates and targets held at RT[6]. In other words, d_e can be a good measure for the droplet formation. However, most of the film depositions by PLA are carried out at elevated substrate temperatures, causing an increase in the target temperature as well. The effect of the target temperature is of interest also from the viewpoint of the ablation mechanism. In this study a correlation between V_d / V_f and d_e for an elevated target temperature was investigated. On the other hand, the size distribution of the droplets can give us helpful information to clarify the mechanisms of laser ablation. A change in the droplet-size distribution was also investigated for a variety of d_e's using the target held at RT and elevated temperature.

The surface roughening in the deposition of Si films by PLA due to an interaction between the ejected materials from the target and the ambient gas during the flight process was reported in our previous paper[7]. This interaction and/or the increase in the substrate temperature may affect the droplet formation on the film surface. In this study effects of both the ambient gas pressure and the substrate temperature on the droplet formation on the films was investigated.

2. Experimental

Films of $YBa_2Cu_3O_X$ (YBCO) and Bi-substituted yttrium-iron-garnet (Bi:YIG) were deposited by PLA. The laser beam was scanned during film deposition. The distance between target and substrate was 35 mm. We assume that there is no essential difference in the surface morphology between YBCO and Bi:YIG films because small differences in the thermal properties, for instance, the melting point, vaporizing point, etc., do not affect the present discussion. The preparation conditions are shown in Table 1. The films prepared were sufficiently thin(0.1 to 0.4 μm) to reduce the experimental error of evaluating the size and volume of droplets because the thick films conceal the droplets below the flat film surface.

Droplet formation on the YBCO film surface was examined by a scanning electron microscope (SEM) for the films deposited in various oxygen pressures. These films cannot be measured by a scanning tunneling microscope(STM) because the surface of the films deposited in a rather high oxygen-pressure was very rough.

The Bi:YIG films with a moderate roughness was characterized by an STM. The volume of droplets over the film was calculated by computer using surface profile data obtained by STM. Each droplet-size (diameter) was determined from each droplet volume by assuming that the droplet shape was spherical. The film volume V_f is the product of the scanned area of the STM measurement and the film thickness determined by a profile tester.

Targets were etched by PLA for 50 seconds(250 shots) to obtain a clear etching profile without the laser beam scanning. Profiles of the etched target were measured by another profile tester. The stylus was scanned along the x direction every 0.1 mm in the y direction in order to evaluate the maximum etching depth d_e.

3. Results and discussion

At first, effects of the elevated substrate temperature and the ambient gas pressure were studied for YBCO films deposited by PLA using ArF excimer laser with a wavelength of 193 nm. Figure 1 shows SEM images of the YBCO film deposited in a variety of oxygen pressures(10^{-4} Pa～40 Pa) at RT with a laser fluence of 4.0 J/cm^2. The morphology of the film surface other than the droplets becomes rough with an increase in the ambient gas pressure. Similarly to Si films[7], the mechanism was discussed as follows. Ejection of particles from the target appears to be roughly independent of the ambient gas pressure. The ejected particles are, however, cooled and loose their kinetic energy by collisions with the molecules in the ambient gas during the flight process, and thus the morphology of the film surface change to be rough due to the solidification of the droplets immediately after reaching the film. The decrease of droplet density in the film by the increase in the ambient-gas pressure as shown in Fig.1 can be explained by the above cooling model, resulting in a reduced sticking coefficient of the droplets on the film surface. On the_contrary, if the substrate temperature is high and droplet cooling is not sufficient, droplets spread and/or migrate on the film, resulting in coalescence of the droplets into the film.

Figure 2 shows SEM images of the surface of YBCO films deposited at a variety of substrate temperatures (RT～740 °C) in an oxygen pressure of 13 Pa with a laser fluence of 4.0 J/cm^2. The density of droplets, especially large droplets, is decreased by increasing the substrate temperature. In this stage two mechanisms are feasible; the change of droplets ejection and/or coalescence of the droplets into the film. Details will be discussed later. In any case, for observation of droplets, an attention should be paid on the preparation conditions such as ambient gas pressure and substrate temperatures.

On the basis of the above results, the size distribution of droplets was investigated for Bi:YIG films prepared at RT by PLA. The result is shown in Fig.3, where the droplet density was normalized by the respective film-thickness in order to eliminate the difference in the amount of deposited material. The value of d_e was varied by changing the laser fluence and wavelength. From Fig. 3 some droplets are found to be several times larger than d_e in diameter, indicating that droplets were possibly formed from spread sheets with d_e due to the surface tension or through a coalescence of small droplets. The increase in d_e is found to enhance the formation of larger droplets in comparison with smaller ones. It has been already reported in our previous paper that V_d / V_f is proportional to $d_e{}^3$ for a variety of ablated materials and laser wavelengths using substrates and targets held at RT[6]. Therefore the increase in V_d in our previous paper is mainly attributed to the formation of larger droplets. This result suggests that a more intense laser fluence contributes to an increase in the molten-layer thickness of the target surface, corresponding to d_e, supporting our previous thermal explosion model[8]. A similar result was obtained also for YBCO films.

Lastly, the influence of the elevated target temperature on the droplet volume was quantitatively investigated. Figure 4 shows a correlation between V_d / V_f and d_e for various target temperatures in Bi:YIG films in 27 Pa oxygen gas. The dashed line in the figure represents the correlation of $V_d / V_f \propto d_e{}^3$ derived in our previous study[6]. The set of the original data in that paper has data scattering with one order of magnitude in V_d / V_f. From this figure it is found that data obtained for the films deposited with a target temperature of 495 °C follow the above correlation within the experimental error. However, the substrate temperature was unintentionally elevated to 430 °C owing to a thermal emission, conduction and convection caused by the increase in the target temperature to 495 °C . This increase in the substrate temperature might cause coalescence of the droplets into the films as shown in Fig.2, resulting in an underestimation of the droplet volume. For examining the above possibility, the pure effect of the substrate-temperature increase was investigated. V_d / V_f for the films deposited at the substrate temperature of 430 °C (closed triangles) is similar to those for RT films (open triangles), suggesting that there is no reduction in V_d / V_f originating from the unintentional increase in the substrate temperature. The result that no coalescence occurred at this temperature different from the result in Fig.2 is probably ascribed to the present higher ambient pressure. Therefore it can be concluded that the correlation between V_d / V_f and d_e is valid for the heated target as well as the RT target.

From the above result it is found that the amount of ejected droplets does not decrease only by increasing substrate temperature. This finding suggests that the depositing droplets on the substrate at the high temperature coalesced into the film, resulting in a decrease in the droplet density on the films surface as shown in Fig.2.

Figure 5 shows the change in the droplet-size distribution for the Bi:YIG films deposited at the target temperatures of RT and 495 °C by PLA with a laser fluence of 7.8 and 11 J/cm^2, respectively. The increase in d_e by the increase in the target temperature enhances the formation of small droplets in comparison with large ones. This origin is not clear in this stage. It was, however, found that the effect of the increase in d_e by the more intense laser fluence is different from that obtained by increasing the target temperature although the correlation between V_d / V_f and d_e does not change.

4. Conclusions

The increase in V_d / V_f caused by increasing d_e due to changes in the deposition conditions using substrates and targets held at RT is mainly attributed to an increase in the droplet formation with a large size. The correlation $V_d / V_f \propto d_e^{\,3}$ is valid also for elevated target temperaures, and an increase in the target temperature enhances the formation of small droplets compared with large ones. On RT substrates, cooling of droplets after the ejection by increased ambient pressure reduces the density of droplets on the film surface because of the low sticking coefficient. In an ambient gas with a low pressure, on the contrary, suppressing the cooling of droplets by the increased substrate temperature also reduces the density of droplets on the film surface due to coalescence of droplets into the film. Thus, for observation of droplets, attention should be paid on the basis of above two opposite mechanisms.

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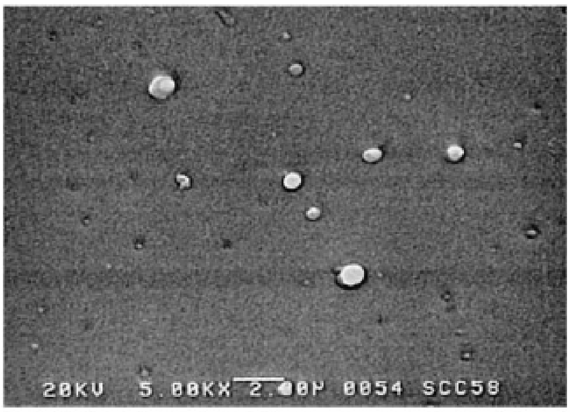
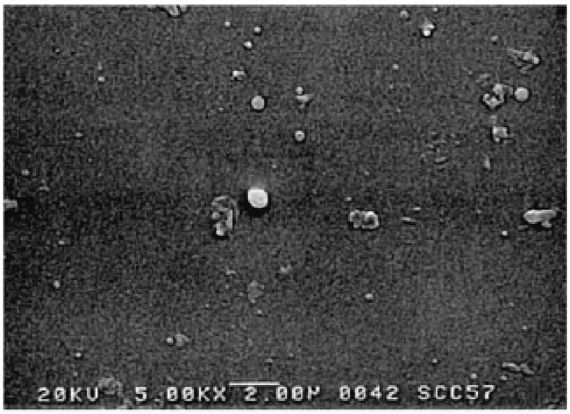
Table 1 Film preparation conditions

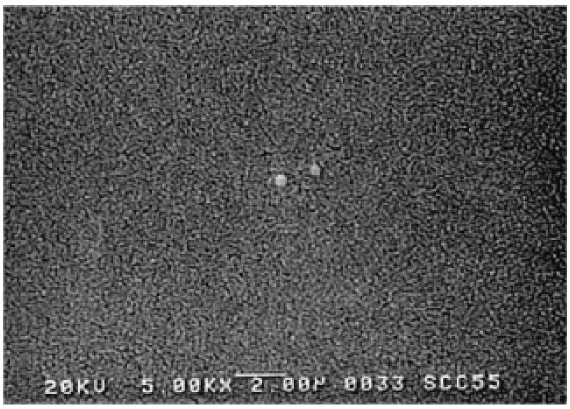
	YBCO	Bi:YIG
Lasers	ArF excimer laser, 193 nm (Shibuya SQL2240)	ArF excimer laser (Shibuya SQL2240) Nd^{3+}:YAG, 355 nm (Continuum 661-10) Nd^{3+}:YAG, 532 nm
Laser fluence	4.0 J/(cm^2 shot)	2.8–21 J/(cm^2 shot)
Laser repetition rate	5 Hz	5 Hz
Ambient O_2 pressure	10^{-4}, 13, 40 Pa	27 Pa
Targets	sintered $YBa_2Cu_3O_x$	sintered $Bi_{1.5}$:$Y_{1.5}Fe_5O_{12}$
Substrates	(100) MgO	Crystal Si
Substrate temperature	RT, 420, 740°C	RT
Deposition time	6–14 min	12–90 min



(a) 10^{-4} Pa



(b) 13Pa



(c) 40Pa

Fig.1. SEM images of the YBCO film surface deposited in oxygen pressures of a)10^{-4} Pa, b)13 Pa, and c)40 Pa. Film deposition was carried out at RT with a laser fluence of 4.0 J/cm^2.

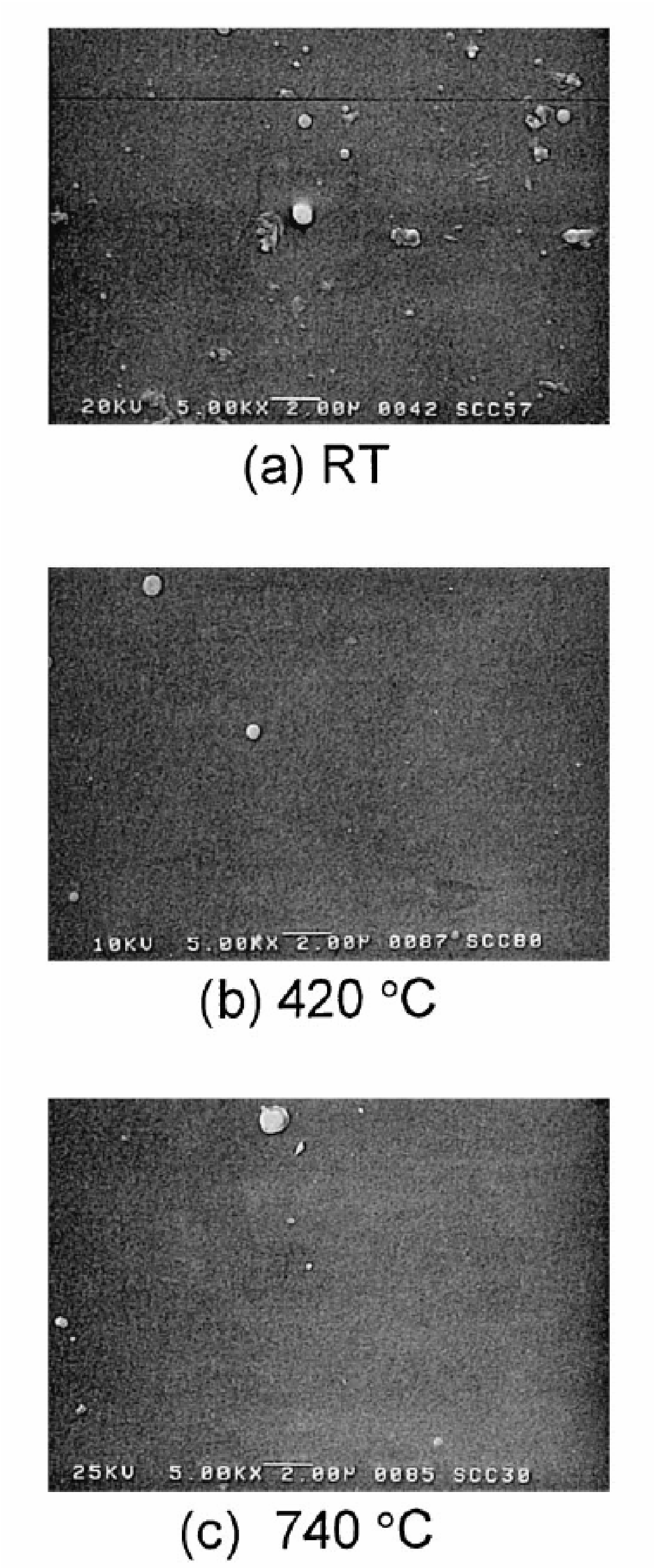


Fig.2. SEM images of the YBCO film surface deposited at substrate temperature of a)RT, b)420 ℃ and c)740 ℃. The film deposition was carried out in an oxygen pressure of 13 Pa for a laser fluence of 4.0 J/cm^2.

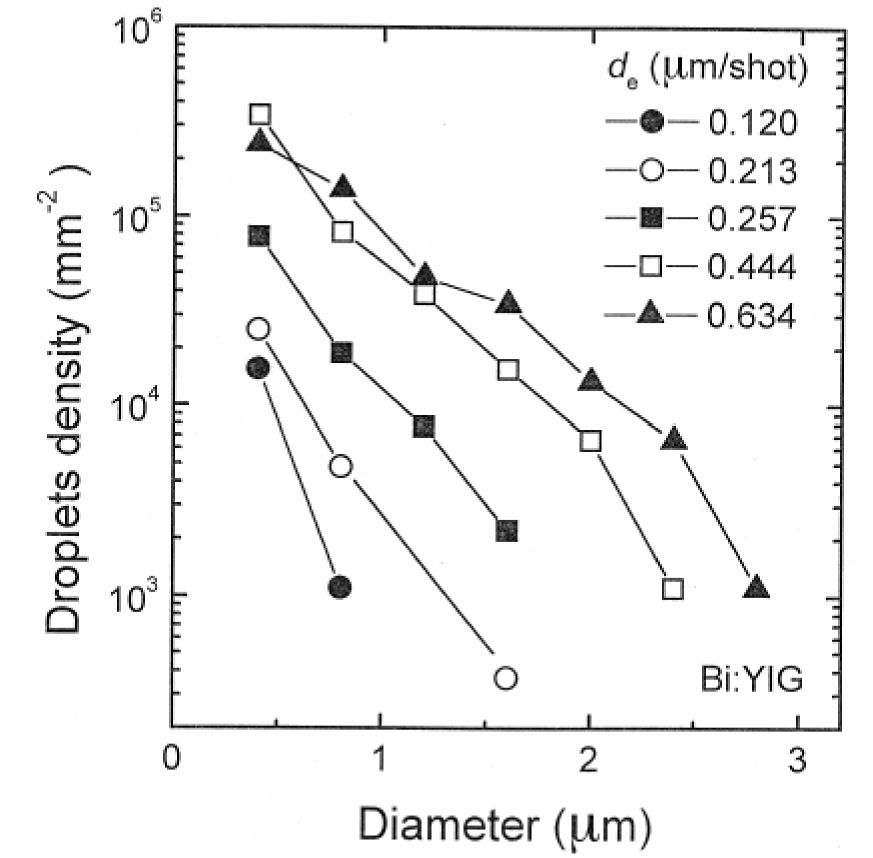


Fig.3. Size distribution of droplets for various d_e's in Bi:YIG films prepared at RT.

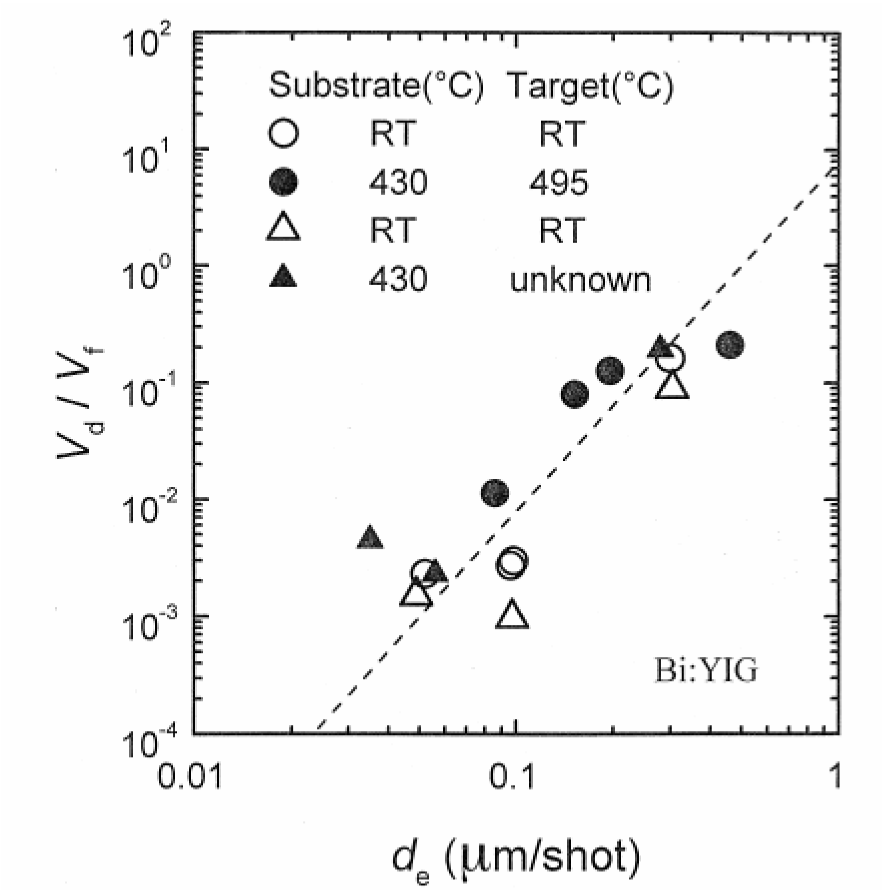


Fig.4. Correlation between V_d/V_f and d_e for various Bi:YIG target temperatures. The slope of the broken line indicates a power of 3 reported in Ref. 6.

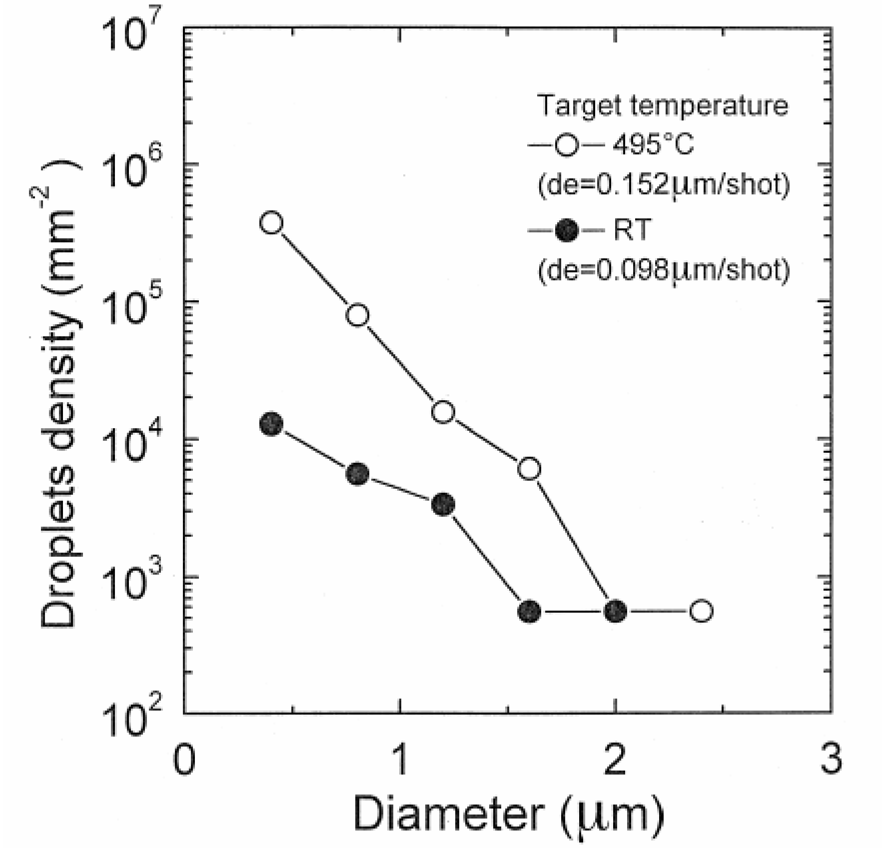


Fig.5. Size distribution of droplets on the films for two target temperatures in Bi:YIG.