Deposition of BaTiO₃ Thin Films by ArF Excimer Laser Ablation

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BaTiO₃ films have been deposited on a quartz substrate at various substrate temperatures by the ArF excimer laser ablation technique. Crystallization of the film deposited at substrate temperatures as low as 300°C was confirmed by X-ray diffraction analysis. The expansion velocities of the laser plume and the ablated species in the plume have also been investigated by time-resolved optical observation and spectroscopy.

1. Introduction

Barium titanate (BaTiO₃) has potential in future electronic applications for use in areas such as high-density dynamic random access memory (DRAM) because of its ability to store a large amount of charge in a small area^(1,2).

BaTiO₃ films are usually deposited by vacuum evaporation and rf sputtering. They require a relatively high vacuum condition due to the principle of operation. Also, the substrate must be heated up to a high temperature in order to obtain crystallized films.

Recently, a pulsed excimer laser ablation method has been widely studied in the fabrication of YBa₂Cu₃O₇⁽³⁾ and other superconducting films⁽⁴⁾. The advantage of the laser ablation method is that it is possible to deposit films at pressures up to a few hundred Pa, including oxygen and other kinds of gases. However, studies of the deposition and characterization of BaTiO₃ films deposited by the laser ablation method have been very scarce.

We obtained crystallized BaTiO₃ films on the quartz substrate at a substrate temperature as low as 300°C without post-annealing.

In this paper, we report spectroscopic and time-resolved optical analyses of the ablation products from an ArF-excimer-laser-irradiated BaTiO₃ target, which provide information on the nature of the ablated species and their expansion velocities. The dependence of film thickness on oxygen pressure and X-ray diffraction patterns of the

BaTiO₃ films deposited on the quartz substrate at various substrate temperatures were also investigated.

2. Experimental Setup

The experimental setup of the laser ablation apparatus is shown in Fig. 1. The ArF laser (lambda Physics, EMG202MSC) gives a 193.3 nm-wavelength beam with a pulse duration of up to 200 Hz and energy of up to 200 mJ/pulse. A spherical lens made of synthetic quartz is used to concentrate the laser beam onto the BaTiO₃ target. The BaTiO₃ target was prepared by the standard sintering method and the stoichiometry was confirmed by X-ray diffraction analysis. The target was rotated at 1 rpm to preclude pit formation on the target surface. All experiments were performed in a stainless steel chamber (10 inches in diameter) evacuated by a molecular turbo-pump backed by a mechanical pump. The maximum pressure of this system was about 1.33×10^{-4} Pa.

The time-resolved optical images of the laser plume were recorded by a streak camera and analyzed by a temporal analyzer.

In the film deposition experiment, the substrate was heated up to 350°C by a resistive heater made of platinum wire. The substrate temperature was measured on the front surface of the quartz substrate by alumel-chromel thermocouple.

UV emission from the plume accompanying ablation was studied by means of a monochromator (Japan Spectroscopic, CT-25C) equipped with a

Fig. 1 Experimental setup of the laser ablation apparatus.

photomultiplier tube (Hamamatsu Photonics, R-106).

3. Observation of the Plume

Time-resolved optical observations of the laser plume of BaTiO_3 were carried out at various oxygen pressures. Laser pulses were focused on the BaTiO_3 target. The plume was viewed normal to its expansion direction and made an image on the monochromator slit, giving a spatial resolution of $100\text{ }\mu\text{m}$ along the target normal.

Figure 2(a) shows a time-resolved optical image of a laser plume obtained by a streak camera at oxygen pressures of 665 Pa. The laser fluence on the target was about 7 J/cm^2 . The vertical axis shows the time and the horizontal axis shows the distance from the surface of the target. The digitized image was stored by a personal computer and analyzed with image-processing software. Figure 2(b) is the three-dimensional plot of the plume shown in Fig. 2(a). This helps to evaluate the detailed features of the plume.

The plume begins at the point of laser beam irradiation on the target toward the substrate as a function of time. Therefore, the gradients of this image give the velocity of the ablated species in the plume. The peak intensity of the plume as a function of time obtained from Fig. 2 is shown in Fig. 3. The maximum intensity appears at $t \sim 50\text{ ns}$, and it decreases exponentially with increasing time.

Figure 4 shows the expansion velocities of the plume as a function of oxygen pressure. From Fig. 2, it is found that the tail of the plume bends. This indicates that the expansion velocity changes with time. We defined two typical velocities. V_1 and V_2 , as shown in Fig. 2(a). The velocity V_1 (shown by a closed circle) is obtained by drawing a straight line on the beginning portion of the plume. This por-

Fig. 2 Time-resolved (a) optical image and (b) three dimensional plot of the laser plume.

Fig. 3 Peak intensity of the plume as a function of time.

tion corresponds to the range between the origin and the maximum intensity of the plume in Fig. 3. The velocity V_2 (shown by the open circles) is obtained from the tail portion of the plume. This portion corresponds to the range after the maximum intensity peak in Fig. 3.

It is found that the velocity V_1 is almost constant ($1.5 \times 10^6\text{ cm/s}$) and independent of the oxygen pressure. On the other hand, V_2 begins to decrease at 100 Pa and quickly decreases as the oxygen pressure increases. The decrease of V_2 may be caused by the scattering of ablated species by oxygen molecules in the chamber. Therefore, the ablated species are strongly affected by the atmosphere near the surface of the substrate at a high oxygen pressure.

4. Thin-Film Deposition

BaTiO_3 films were deposited on the quartz substrate at various deposition conditions. The

Fig. 4 Expansion velocity of the plume as a function of oxygen pressure.

Fig. 5 BaTiO₃ film thickness as a function of oxygen pressure.

substrates (1 mm thick, 10 × 10 mm) were cleaned with trichloroethylene, acetone, ethanol, and deionized water. The distance d between the target and the substrate was varied from 4 to 6 cm. The film was deposited at the substrate temperature, in the range from room temperature to 350°C. Oxygen gas was introduced into the belljar, and pressure inside the chamber was varied from 10^{-3} Pa to 10^2 Pa in this experiment.

In Fig. 5 we show the BaTiO₃ film thickness deposited at room temperature as a function of oxygen pressure. It can be seen that for pressures greater than 1 Pa, the film thickness decreases. Here, n/n_0 , shown by the solid line in Fig. 5, is the fraction of molecules which have not collided with others after traveling a free path of length d . Since intermolecular collisions are statistical events, the actual free paths vary. Their distribution is given by an exponential decay function $n/n_0 = \exp(-d/\lambda)^5$, using mean free path λ . The calculated curve

Fig. 6 X-ray diffraction patterns of BaTiO₃ films deposited at substrate temperatures of 250, 300 and 350°C.

Fig. 7 Optical micrograph of BaTiO₃ film deposited at the substrate temperature of 350°C.

shows a good agreement with the data. This fact indicates that the reduction of film thickness is due to the collision of ablated species with gas molecules.

Though the laser ablation technique is essentially free from restrictions regarding the pressure of the atmosphere, it is necessary to deposit the film at a pressure of less than 0.1 Pa in order to obtain thick films.

Figure 6 shows the X-ray diffraction patterns of BaTiO₃ films deposited at substrate temperatures of 250, 300 and 350°C. The deposition pressure for these samples is 2.7×10^{-3} Pa. The films deposited at 250°C or less were presumed to be amorphous since no diffraction line could be observed. Films deposited at substrate temperatures higher than 300°C were polycrystalline with (101), (110) and (002) orientations.

Figure 7 shows the optical micrograph ($\times 100$)

Fig. 8 Emission spectrum of the laser-induced plasma in the wavelength range of 200 to 320 nm.

of BaTiO₃ film deposited at the substrate temperature of 350°C. Clear mosaic block patterns are observed. However, the patterns were not as clear for the samples deposited at 200°C, and no patterns were observed for the samples deposited at room temperature. The appearance of such patterns may be due to crystal growth from different nucleation sites or the mismatch of thermal expansion coefficients between the film and the substrate⁶. The thermal expansion coefficients of quartz glass and BaTiO₃ are 5.6×10^{-7} and $6 \times 10^{-6}/^\circ\text{C}$, respectively.

In order to probe the components of laser-ablated plasma, spectroscopic measurements were carried out in the wavelength region from 200 to 500 nm. A typical emission spectrum of the laser-induced plasma in the wavelength range of 200 and 320 nm is shown in Fig. 8. It is found that the principal emission lines between 200 and 500 nm arise from Ti, Ba and oxygen lines.

These results indicate that the elements of the film deposited by ArF laser ablation technique are highly excited species. Therefore, their internal energy can be released into the migration energy on the surface of the substrate, and the crystallinity is improved.

It is reported that a substrate temperature higher than 500°C is necessary for the BaTiO₃ films to crystallize⁷. Otherwise, they become amorphous. It can be thought that high-level excitation of the species by laser ablation resulted in the decrease of

the substrate temperature for crystallization.

5. Conclusions

Polycrystalline BaTiO₃ films were grown on quartz substrates by the ArF excimer laser ablation method at substrate temperatures as low as 300°C. The expansion velocities of the laser plume were obtained, and the spectroscopic analysis of the ablation products from the ArF-excimer-laser-irradiated BaTiO₃ target indicated that the majority of lines originated from excited Ti and Ba.

In the excimer laser ablation for the BaTiO₃ film deposition, excited and/or ionized atoms of ablated species are supplied on the growing film. This is very effective for the crystallization of the materials. Further work is in progress at our laboratory.

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