Bi₂Sr₂Ca₁Cu₂O_x Thin Film Deposition by Q-switched YAG Laser

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The fourth harmonics of Q-switched YAG was used to deposit Bi₂Sr₂Ca₁Cu₂O_x (Bi-2212) films on MgO[100] substrates. A secondary function generator was employed to modulate Q-switch while the primary generator was synchronized with flash lamps to decrease the repetition rate of laser beam. At the rate of 2 Hz, the beam energy increased ~50% per pulse and the fluctuation of power stayed in ±2% during the deposition. In order to decrease the number of particles on film, targets were irradiated by the laser before deposition. Using the fourth harmonics of slower Q-switch YAG, epitaxial growth of Bi-2212 was achieved on MgO[100] substrate with the transition temperature of 72 K. Comparing the results with those deposited using an excimer laser, higher oxygen pressure was required to obtain epitaxial growth of Bi-2212.

Introduction

The development of electronic devices requires high quality single crystal film with low defect density and a flat surface. Fine control of atomic layer is also required in order to fabricate multilayer. Multilayered structure has an advantage on investigating the thin film, it allows X-ray to estimate layer thickness, roughness and mass density.

A variety of methods have been used to deposit high quality thin films and multilayer structure, such as sputtering,^{1,2)} molecular beam epitaxy (MBE)^{3,4)} and pulsed laser deposition (PLD). The PLD method is an extremely simple technique, and one of the most versatile methods for growing thin film including multilayer structures. With an appropriate laser and a choice of target materials, any kind film can be deposited by PLD method. Unlike MBE, simply replacing targets allows the system to be ready for new materials. The deposition conditions also have flexibility. Sputtering must take place under plasma conditions, the PLD method can be carried out from high vacuum to high pressure of several hundreds Pa in the atmosphere of any gas.

Most of the works on PLD have been done using an excimer laser as ultraviolet (UV) source.⁵⁻⁸⁾ YAG

laser has mainly been used as a source of visible and infrared (IR) laser investigating the effect of wavelength used for PLD. The significant disadvantage in use of YAG is the smaller laser power in UV range, compared to the excimer laser. YAG has large IR power. Using a nonlinear crystal to obtain UV, the efficiency of power conversion is only 15% relatively to fundamental (IR). YAG does not require fluoride like the excimer laser, since YAG is a gas-free laser and solid-state system.

Excimer laser also has freedom of repetition rate. Simply adjusting frequency of voltage for electrode in gas chamber allows repetition to be set up. Unlike the excimer, optical adjustments are required on YAG system in order to change the repetition rate. Loss of power is caused by optical mismatch. In this study, another function generator was employed to modulate only the Q-switch while flash lamps were modulated at the original rate (slower Q-switched YAG),⁹⁾ and Bi₂Sr₂Ca₁Cu₂O_x (Bi-2212) thin film was deposited on MgO[100] substrates by using of the fourth harmonics of slower Q-switched YAG laser.

Experimental Procedures

Bi-2212 targets were made from stoichiometric amounts of Bi₂O₃, SrCO₃, CaCO₃ and CuO pow-

Fig. 1 Schematic diagram of pulsed laser deposition. Four targets can be attached on the holder, which swung during the deposition so the laser scanned over the target.

ders. The mixture of powders was ground, and calcined for 2 hours in oxygen atmosphere at 800°C, and pressed as pellets at the pressure of 400 kgf/cm², then sintered again in oxygen atmosphere at 800°C.

Up to four targets can be attached on target holder. The target holder allowed laser beam to scan the surface of target by swinging during deposition. The targets can be switched by rotating holder during each depositions so that thick film can be deposited by rotating targets continuously in the vacuum chamber. Multilayered structure can also be fabricated continuously in the vacuum environment. MgO[100] substrates were glued on a heater block with silver paste, and placed in front of the target with distance (d_{sub}) from 35 to 50 mm. The oxygen pressure was also varied from 20 to 120 Pa. The incident beam was irradiated on the target at angle of 45° normal to target surface.

The laser system used in this study was a Gaussian type Q-switched Nd:YAG laser (Spectron Laser Systems SL803G). The fourth harmonic of 266 nm was used to deposit Bi-2212 film with the repetition rate of 2 Hz by using slower Q-switched YAG system. After deposition, crystal structure examined by X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED), and the transition temperature T_{c0} ($R=0$) was measured by the van der Pauw method. The thickness and roughness were estimated using X-ray reflectivity (XRR). The surface roughness of films was also observed by atomic force microscopy (AFM). Scanning electron microscopy (SEM) was employed in order to observe the surface of target irradiated by laser beam after deposition. **Fig. 1** shows schematic diagram of PLD method using the fourth harmonics produced by slower Q-switched YAG.

Results and Discussion

The repetition rate of 10 Hz was applied to the YAG system to deposit Bi-2212 films. The results of XRD and RHEED measurements showed c-axis orientation growth, but not epitaxial growth. Some samples showed T_{c0} around 65 K, though lots of samples stayed in low T_{c0} . With small energy per pulse, the range of oxygen pressure was limited to low pressure to generate an appropriate plume on the target. The beam power increased to ~70 mJ/pulse at repetition rate of 2 Hz with slower Q-switch, instead of 40 mJ/pulse at rate of 10 Hz. The primary function generator modulates two flash lamp with the repetition rate of 10 Hz, and the secondary function generator is synchronized with the primary generator with the repetition rate of 2 Hz. The secondary generator has the duration of 450 ms, so that it picks up a pulse only every fifth pulse from the primary generator. Adjusting the duration time of the secondary generator gives the choice of repetition rate on the PLD system (**Fig. 2**).

With d_{sub} of 50 mm, T_{c0} around 60 K was obtained on film deposited in a wide range between 50 to 110 Pa of oxygen atmosphere. In the case of $d_{sub} = 35$ mm the film showed c-axis orientation, however, polycrystal structure was obtained by RHEED image. Epitaxial growth was verified by XRD on Bi-2212 film deposited at the substrate temperature of 750°C. **Fig. 3** shows XRD pattern on Bi-2212 film deposited at the oxygen pressure of 60 Pa with $d_{sub} = 40$ mm, and the ϕ scan using Bi-2212 (1122) peak is shown in **Fig. 4**. Compared with the ϕ scan on MgO substrate using MgO(113) peak, Bi-2212 film was grown epitaxially with a and b axes parallel to those of MgO[100] substrate (cubic on cubic). T_{c0} of 72 K was obtained on *as-grown* Bi-2212 film (**Fig. 5**). The T_{c0} was relatively low value, however, without any buffer layer $T_{c0} \sim 70$ K was often obtained on MgO[100] substrate.¹⁰⁾

One of the major disadvantages of using PLD method is the particulate generated from target. With hand-made target, "pre-ablation" may be one of most effective methods. The target was irradiated in chamber before deposition. The surface topology was examined by AFM. **Fig. 6** and **7** show AFM images of top surface of Bi-2212 films deposited on MgO[100] with and without pre-ablation, respectively. The average roughness (R_a) of ~3 nm was estimated from the AFM image. The surface roughness was also estimated by XRR measurements, and the roughness of ~3 nm was

Fig. 2 The primary generator modulates only the flash lamp. The secondary generator synchronized with the primary generator modulates only Q switch. The repetition rate of the system was changed by adjusting the duration time of the secondary generator.

Fig. 3 X-ray diffraction pattern of a $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ film deposited on $\text{MgO}[100]$ at the substrate temperature of 750°C with oxygen pressure of 60 Pa.

Fig. 4 ϕ scan on $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ film deposited on $\text{MgO}[100]$ substrate at 750°C substrate temperature at oxygen pressure of 60 Pa. Using peaks of Bi-2212 (1122) and $\text{MgO}(113)$.

Fig. 5 The transition temperature of 72 K was obtained on $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ film deposited at 750°C substrate temperature at oxygen pressure of 60 Pa.

Fig. 6 AFM image of the surface on epitaxial $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ film without pre-ablation. The film thickness was estimated at 700 Å.

obtained by the fitting simulation, which showed good agreement with AFM image (Fig. 7).

The surface of target was also examined by SEM (Fig. 8). The surface morphology depends on the laser energy irradiating the target.⁸⁾ The laser power generated by YAG is small compared to excimer laser although peak power (energy/duration time) is relatively larger than excimer laser. A power density of $\sim 0.5 \text{ GW/cm}^2$ is usually required by the wavelength of ultra violet in order to generate congruent deposition on YBaCuO .⁸⁾ The power density of only $\sim 0.14 \text{ GW/cm}^2$ was obtained by using of slower Q-switched YAG though, as seen in Fig. 8, cone structure was formed on surface on the target.

Fig. 7 AFM image of the top surface on epitaxial $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ film with pre-ablation of 3 min. showed the average roughness of ~ 3 nm.

Fig. 8 SEM image of surface of Bi-2212 target irradiated by the fourth harmonics of YAG laser for 3 min.

With Bi-2212 target and the power density of ~ 0.14 GW/cm², the deposition must be carried

out in congruent conditions.

Conclusion

In summary, high and stable power was obtained by using the fourth harmonics generated by slower Q-switched YAG laser. The YAG laser generates relatively low energy, however, the laser power was significantly increased by applying slower Q-switch method. With the slower Q-switched YAG along with pre-ablation of target, the epitaxial films of Bi-2212 were deposited on MgO[100] substrates.

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