Bi₂Sr₂Ca_{n-1}Cu_nO_y superconducting films deposited by rf magnetron sputtering under magnetic field

Naoki Fujiwara, Takahiro Onishi, Koji Katsurahara and Satoru Kishida

Tottori University, 4-101, Koyama-minami, Tottori 680-8552, Japan Fax: 81-857-3-5244 TEL: 81-857-31-0880 e-mail: b99t3055@maxwell.ele.tottori-u.ac.jp

We deposited $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (Bi-based) superconducting thin films by rf magnetron sputtering method under magnetic field. The Bi-based thin films showed superconducting transition at about 40K without any annealing process for the oxidization of them. In addition, the optimum substrate temperature for obtaining Bi-based single-phase films was decreased by applying magnetic field. Therefore, applying magnetic field during film deposition is useful for high quality Bi-based films.

Key words: under magnetic field, without annealing process, oxidization, valency of Cu

1. Introduction

 $Bi_2Sr_2Ca_{n-1}Cu_nO_v$ (Bi-based) [1] and $YBa_2Cu_3O_v$ (Y-based) [2] are copper oxide material. Especially, Bi-based superconductors have high critical temperature and a low pollution material. In order to apply superconductors into electronics, it is necessary to prepare high quality Bi-based films, since the performance of the devices is dependent on their quality. The valency of Cu is related to superconducting property. Mother body of Bi-based superconductors is known to be antiferromagnetism and Mott insulators. Therefore, the superconductivity of the Bi-based superconductors is dependent on the hole concentrations introduced by oxidization [3-4]. In addition, it was reported that the optimum gas pressure and substrate temperature for obtaining Bi₂Sr₂Ca₂Cu₃O_v (Bi-2223) single-phase films were 100mTorr and 720℃ in rf magnetron sputtering method, respectively [1].

In this study, we deposited Bi-based thin films by rf magnetron sputtering method under magnetic field, and investigated the effect of the magnetic field on the



magnetic field

growth and the characteristics of the films. This is the first report on the growth of the Bi-based films in rf magnetron sputtering method under magnetic field.

2. Experimental

Fig.1 shows the diagram of our rf magnetron sputtering apparatus and the configuration of four magnets. (a) and (b) represent a top view and a side view of our system. Four magnets with the magnetic field of about 1T were used in this study. Targets and



Fig.2 Geometry of target and substrate in our sputtering system





substrates were put in off-axis geometry to suppress re-sputtering effect of substrates. The substrates were heated by Si heater, where the current directly flowed in Si.

Fig.2 shows the geometry of the target and the substrate. We used a mixture gas of He and O_2 as a sputtering gas. By the use of He gas, active oxygen particles of O^{2+} and O^+ are effectively produced. In this case, the O^{2+} particles sputter the targets.

The Bi-based films were prepared changing substrate temperatures, gas pressures and gas ratios. The target composition was Bi:Sr:Ca:Cu=3:2:2:3. The deposition time, the rf power, the substrate temperature and the gas pressure were 2h, 150W, $660 \sim 740$ °C and 50mTorr ~ 300 mTorr, respectively. The gas ratios He:O₂ were 4:1 and 3:2.

The films were measured by X-ray diffraction analysis (XRD) and resistance-temperature characteristics (R-T), which is a standard 4 probe method. In addition, the as-deposited films were annealed in O_2 gas flow at 500° or 800° .

3. Results and discussion

3.1 Dependence of substrate temperatures

Fig.3 shows XRD patterns of the Bi-based films deposited at various temperatures, where the sputter gas pressure and the gas ratio are 100mTorr and He: O_2 =4:1, respectively. As shown in the figure, the peaks were observed at about 23.7, 28.7 and 33.6°, which are assigned to (0010), (0012) and (0014) from a Bi-2223 phase superconductor. This indicated that all the films were approximately Bi-2223 phase and c-axis-oriented. Therefore, the Bi-2223 phase films were able to be prepared at the substrate temperatures of about 700°C. The notation of 740℃ represents the XRD pattern of the Bi-2223 phase film deposited at 740℃ without applying magnetic field. When the magnetic field was not applied during film deposition, the optimum substrate temperature for obtaining Bi-2223 phase films was about 740℃. As shown in Fig.3, the optimum substrate temperature for Bi-2223 phase films was about 700° . Therefore, the optimum substrate temperature for Bi-2223 single-phase films decreased by 40° when the magnetic field was applied during film deposition.

Fig.4 shows R-T characteristics of the Bi-based films deposited at the substrate temperatures of $660 \sim 740$ °C. As shown in the figure, the film deposited at 700 °C showed a metallic temperature dependence of resistance in the normal state and a superconducting critical temperature (Tc) at about 40K. This result was the first report on the as-deposited Bi-based films with the Tc in rf magnetron sputtering method. However, the previous report [1] without applying magnetic field indicated that the as-deposited Bi-2223 phase films never showed Tc in a temperature range of $20 \sim 300$ K. Here, the as-deposited Bi-based film with the Tc of about



Fig.4 R-T characteristics of the films as-deposited at 660~740°C



Fig.5 R-T characteristics of the films annealed at 500°C after deposition at 700 and 740°C

40K were obtained. This may be explained by the oxygen contents in the film, which is caused by applying magnetic field during film deposition. From the results, we found that the optimum substrate temperature for obtaining the Bi-based films with high Tc was about 700° C. Although the film deposited at 740° C and 660° C showed abrupt decrease of resistance at about 50K and 70K, respectively, it did not show zero-resistance temperature in temperature range of our measurement.

Fig.5 shows the R-T characteristics of the Bi-based films post-annealed at 500° C for 0.5h in oxygen gas flow. The films deposited at 700 and 740°C showed a metallic temperature dependence of resistance in the normal state, and their Tc were about 73K. From the results, we found that the Tc of the films increased by annealing at 500° C in oxygen gas flow, and that the Tc of the post-annealed films were independent of substrate temperatures.

Although the figures were not shown, the films were post-annealed at 800° for 0.5h in air. The film



in various gas pressures

deposited at 700° showed two critical transitions, where the resistance abruptly decreased at about 110K and became zero at about 83K. However, the films did not show the temperature of about 110K although the post-annealing was carried out.

3.2 Dependence of sputter gas pressure

Fig.6 shows XRD patterns of the Bi-based films deposited in the gas pressures of 50 to 300mTorr, where the substrate temperature and the gas ratio are 700 °C and He:O₂=4:1, respectively. As shown in figure, the film deposited in 100mTorr was Bi-2223 single-phase, whereas the film in 50mTorr was like a Bi₂Sr₂Ca₃Cu₄O_y (Bi-2234) phase, which is estimated by the distance among XRD peaks. The film deposited in 300mTorr was Bi-2212 single-phase. From the results, we found that the superconducting phases of the films were controlled by gas pressures during film deposition, and that the number of Cu-O layers n decreased with increasing the gas pressures. It is interesting in getting the Bi-2234 phase film, since there were hardly reports on the characteristics of the Bi-2234 film.

Fig.7 shows R-T characteristics of the as-deposited Bi-based films prepared in the gas pressures of 50 to 300mTorr, where the substrate temperature and gas ratio are 700°C and He:O₂=4:1, respectively. As shown in the figure, the film deposited in 100 and 300mTorr showed a metallic temperature dependence of resistance in the normal state, and their Tc were 40K and 55K, respectively.



Fig.7 R-T characteristics of the films deposited in various gas pressures

However, the resistance of the film deposited in 50mTorr abruptly decreased at about 30K, although it did not show zero-resistance. From the results, we found that the Bi-2212 single-phase film was prepared easier than the Bi-2223 or the Bi-2234 phase films.

We carried out the post-annealing of the films deposited in various gas pressures. Although the figures were not shown, the films deposited in 50, 100 and 300mTorr and annealed at 500° C in oxygen gas flow showed zero-resistance temperatures. Therefore, we found that the superconducting properties of the Bi-based films were improved by annealing at 500° C.

4. Conclusions

We deposited $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (Bi-based) superconducting thin films by rf magnetron sputtering method under magnetic field. The Bi-based thin films showed superconducting transition at about 40K without any annealing process for the oxidization of them. In addition, the optimum substrate temperature for obtaining Bi-based single-phase films was decreased by applying magnetic field. Therefore, applying magnetic field during film deposition is useful for high quality Bi-based films.

Acknowledgment

We use NEOMAX that is provided by SUMITOMO SPECIAL METALS CO.,LTD. We thank this company. References

[1]M Ogura, K Matsumoto, K Katsurahara and S Kishida :Supercond. Sci. Technol. 15 (2002) 1757-1759.

[2]Yanwei Ma, Kazuo Watanabe, Satoshi Awaji, Mitsuhiro Motokawa : Journal of Crystal Growth 223(2001) 483-489.

[3]M.Opel, R.Nemetschek, F.Venturini, R.Hackl, A. Erb,
E. Walker, H.Berger and L. Forro : phys. stat. sol. (b)
215, 471 (1999) 471-476.

[4]J. S. Lee, Y. S. Lee, K. W. Kim and T.W.Noh : physical review B, Vol.64, 165108.

(Received October 13, 2003; Accepted July 1, 2004)