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Process Characteristics for $YBa_2Cu_3O_{7-d}$ Films Fabricated by Single Target Sputter and Surface Modification Technique

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Abstract Thin films of $YBa_2Cu_3O_{7-d}$ were prepared on various substrates of MgO(100), $SrTiO_3$, and $LaAlO_3$ by using off-axis magnetron sputtering methods and annealing in-situ. The parameters of film fabrication processes had been optimized through a "follow the local maxima" strategy to yield good quality films in terms of the critical temperature T_C and the critical current density J_C. Optimized processes employing a plane magnetron and an cylindrical magnetron yielded $T_C > 90K$ along with $J_C > 10^6$ A/㎝² at 77K and $> 2 \times 10^7$A/㎝² at 5K.

The samples, however, showed degradation in the properties, after chemical etching for fabrication of microbridges with the line width of 2–10 microns. In particular, the value of T_C for the microbridges of 2 microns was as small as 80%. The degradation was strongly dependent on the line width through a formula : $T_C(e) = T_C(b)\ \{1 - a\ \exp(-1000\ bL)\}$ where $T_C(e)$ and $T_C(b)$ are the values of T_C in the absolute scale measured after and before chemical etching, respectively and L is the line width in mm. By utilizing a best fitting technique, the proper constant values of a and b were found as exp(−1.2) and 0.22, respectively. This formula was very useful in estimating the upper limit of the device operation temperature.

1. Introduction

Superconductors, due to their unique electromagnetic properties, would be well commercialized in wide application areas if their superconducting critical temperatures (T_C) were high enough to avoid conventional expensive coolants, e.g. liquid helium. Although room temperature superconductors would remain yet in fantasy, microelectronic devices consisted of relatively high T_C superconducting (HTS) materials utilizing an inexpensive coolant, e.g. liquid nitrogen (boiling temp. 77K), are expected to become popular in the near future. Liquid nitrogen costs a hundred times cheaper than its rival and also possesses about a hundred times higher cooling power ; total expenditure becomes only a ten-thousandth. New superconducting materials including Y-base compounds have displayed their characteristics superb, not only in the values of T_C but also in the values of critical current density J_C and critical magnetic field H_C.

Thin films of these so called HTS materials have been actively studied and employed in the proto-type1) microelectronic devices such as superconducting quantum interference devices (SQUIDs), microwave resonators, and electromagnetic filters. Researchers at IBM2) suceeded to make the first dc-SQUID using $YBa_2Cu_3O_{7-d}$ thin films of which grain boundaries behave as weak links between the superconducting grains. Grain boundary junctions, advanced from that idea, have been further developed in the forms of bi-crystals,3) bi-epitaxial junction4), edge junction,5) step-edge junction6), etc. For these devices, film deposition and etching technologies to fabricate microbridges and Josephson Junctions have been the essential portion during their development periods.

Since $YBa_2Cu_3O_{7-d}$ possesses a strong anisotropy, the superconducting films for such samples would be preferable to form along the c-axis epitaxially during the deposition. For this purpose, several techniques and substrates have been employed. Popular deposition methods[7] would include sputtering, co-evaporation, laser ablation, and chemical vapor deposition, and recently even molecular beam epitaxy has been also mobilized. In consideration of direct commercialization, single target sputtering method has been selected for deposition work because this would render a good potential to process large enough work pieces with high uniformity and reproducibility in surface conditions. Even though recently an on-axis sputtering method successfully produced[8] $YBa_2Cu_3O_{7-d}$ superconducting multilayer films, off-axis techniques had been well established owing to their obvious process advantages.[9, 10] Hence, we have started with equipments prepared just to do this by off-axis method. Such widely used substrates as MgO, $SrTiO_3$, and $LaAlO_3$ were chosen for comparison. It is noted, though, that $SrTiO_3$ and $LaAlO_3$ are expensive materials and the dielectric constant of $SrTiO_3$ is too high (e=1900 at 77K) as for an electronic device. The commercialization being kept in mind, MgO would be the best choice if the $YBa_2Cu_3O_{7-d}$ film that has been deposited on it showed reasonably good characteristics ; the emphasis was placed, therefore, on this material throughout the work. And also an inexpensive chemical etching as a form of surface modification process was supposed to follow for manufacturing microbridges. However, it was noted[7] that the superconducting film characteristics including T_C became degraded after chemical etching. The degradation might hinder the whole project. To understand it better, quantification has been necessary before pushing the feasibility to the limit, i.e. the line width about 1 micron.

2. Experimental Set-up

For the single target magnetron sputtering, various targets[7] with chemical compositions of $YBa_2Cu_xO_y$ where $3 \leq x \leq 6$ were employed to produce $YBa_2Cu_3O_{7-d}$ sample flims. The MgO substrates with a polished surface ensuring its roughness 〈100 nm were treated in a series of ultrasonic cleaning baths with acetone and ethanol, consecutively, each for 15 seconds. During the in-situ fabrication process, the substrate temperatures have been kept within a range between 600 and 850℃. The plane magnetron set-up is reported in ref. 7, along with the deposition conditions and procedures, in detail. Another unit equiped with a hollow cathode type target, so called inverted cylindrical magnetron sputtering (ICMS) has also been employed[11] in an effort to improve the deposition rate. For this equipment, a dc power supply with a capacity of 1㎾ was utilized. The procedures for both film preparation techniques are well described in ref. 12. The base pressure of vacuum chamber was kept as 10^{-6} Torr by using a diffusion pump, before Ar and O_2 gases were introduced up to 100-350 mTorr for the deposition process and the diffusion pump was turned off leaving only the rotary pump on. The partial pressure of Ar was allowed as 80 to 250 mTorr and the ratio between the two gases was adjusted as 2-4. The substrate temperatures were maintained within a range of 700-770℃. With a bias voltage varying between 145 and 160V (the equipment power 45-75W) and the distance between the substrate and the bottom of cylindrical target within a range of 20 to 30㎜, the deposition process was continued for 40-180 minutes to produce a film thickness of 200-600 nm with which the film growth was calculated as 2-5 nm/min in average. After deposition, oxygen was introduced into the vacuum chamber for its partial pressure up to 600 Torr until the specimens were cooled quickly to 450 ℃ in 20 minutes and kept there for one hour, then cooled down to the room temperature. The experimental procedures for $YBa_2Cu_3O_{7-d}$ films to be deposited on $SrTiO_3$ or $LaAlO_3$ were described else where (see References 12 and 16 for details). After deposition, each sample was examined to clarify its characteristics in terms of T_c and J_c afterwards.

The specimens after film deposition went through microbridge patterning processes for the line width down to 2 micrometers, using a conventional photolithography and a chemical etching technique, as shown in Fig. 1. The microbridges to measure the value of J_c were designed to possess the width and length of 0.5 and 1.0㎜, respectively. To select an appropriate etchant, 1-5% phosphoric acid,[6] 2% nitric acid[3], and saturated etylene-diamine-tetra-acetic acid (EDTA) solution were tried. The critical current flowing through a microbridge was directly measured, using a standard four-probe method. For this set-up, a Nanovoltmeter (keithley Model 181) and a power supply unit (Keithley Model 224) were employed.

3. Results and Discussion

Sputter Deposition for $YBa_2Cu_3O_{7-d}$ Thin Films

While various composition targets[7] were tried to obtain the stoichiometric thin film with the relatively high value of T_c, we found for the plane magnetron process that the composition ratios of Ba/Y and Cu/Y to be 1.8 and 3.7, respectively, produced best results. The film samples, however, displayed some apparent second phase particulates under SEM (scanning electron microscopy) examinations (see Fig. 2 for a typical micrograph). This type of microstructural problem became solved when a target with 123 composition ratio was employed and the deposition parameters have been studied to determine the optimal conditions. The main characteristics would be definitely related with the sputtering gas pressure P_{total} and the distance from substrate to target D_{s-t}. The pressure needed higher than 100 mTorr to render a proper mean free path, resulting the film product composition same as the target. Then, in order to compensate the lowered deposition rate due to the increase of gas pressure, the value of D_{s-t} should be smaller than 60㎜. Pre-experimental runs with a 123-target confirmed that the proper value of P_{total} must remain within a range from 100 to 300 mTorr as combined with a $D_{s-t}=40$(horizontal)+42(vertical) ㎜.

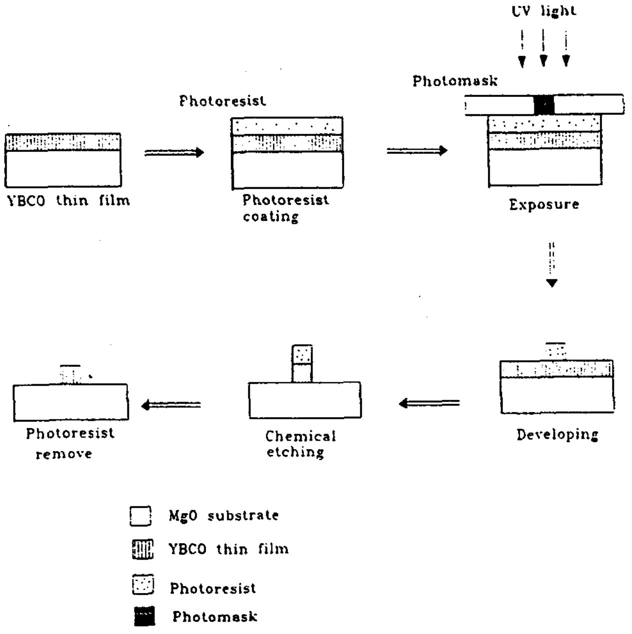

Fig. 1. Patterning process of YBCO film by photolithography and chemical etching.

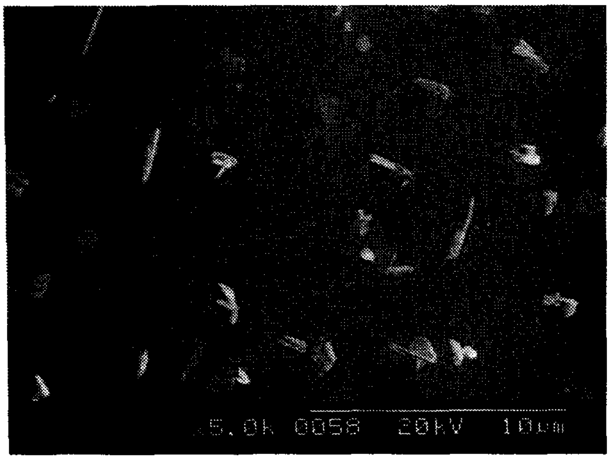

Fig. 2. SEM micrograph of the film deposited under the pressure of 200 mTorr.

Table 1. T_{sub} Varied for Sputtering Process Optimization Scheme (P_{total}=200mTorr, Ar/O_2 Ratio=3, Power=110 W, D_{s-t}=40+42㎜)

T_{sub}(℃)	740	750	755	760	765	770	780
Bias(V)	44.5	21.6	18.0	19.1	18.2	17.6	20.0
T_c(K)	62.8	83.0	83.1	84.2	84.3	85.0	72.1

"Follow the local maxima" strategy was utilized to find the optimized condition for the best resuting Tc; firstly a set of experimental runs were carried on with a major parameter varied within a reasonable range while others fixed to find the local best in T_C, then the second parameter was varied, etc. In this optimization scheme, first the substrate temperatures for MgO were varied within a range of 740–780℃. Table 1 shows the values of T_{sub} and the corresponding proper self-induced dc-bias voltages that ranged between −17.6 and −44.5 volts during each deposition run. For this set of experiments, other parameters than T_{sub} were fixed as ; P_{total}=200mTorr, Ar/O_2 Ratio =3, and Power=110W. The thickness of the films was kept constant at 200 nm throughout this work. The averages of T_C values measured after each run are shown also in the table. It is obvious here that the first local maximum T_C= 85K has occured at T_{sub}=770℃.

Next set of experiments was carried out with the values of Ar/O_2 gas ratio varied within a range of 1 to 15, fixing T_{sub} as 770℃ but the rest parameters same as the first set. During this experimental period the bias ranged from −10.0 t0 −20.1 volts, which is arranged for each case in Table 2 along with the resulting T_C value. Table 2 clearly depicts the second local maximum T_C=86.3K to have occurred with a ratio Ar/O_2=9.

Final set of experiments for the optimization scheme was run varying the chamber pressure P_{total} within a range of 100–300 mTorr and keeping Ar/O_2=9. The bias was varied from −23 to −12 volts as P_{total} increased. The data of T_C obtained from these samples are plotted against the corresponding P_{total} values in Fig. 3.

Table 2. Ar/O_2 Gas Ratios Varied for the Sputtering Prcoess Optimization(T_{sub}=770℃, P_{total}=200mTorr, Power=110W, D_{s-t}=40+42 mm)

Ar/O_2	1	3	5.5	9	12	15
Bias(V)	20.1	20.0	12.6	11.5	10.2	10.0
T_C(K)	85.0	85.4	85.5	86.3	84.9	17.0

As shown in Fig. 3, the final maximum T_C as 90K has been reached when P_{total} was kept at 150mTorr. It is important to point out that −20V dc bias was possible for the run to obtain good film surface condition. From the samples examined under an SEM, we observed excellent surface morphology wihout much visible features around. This would affirm the high quality of film product. In addition, YBCO films[7)] synthesized on MgO with ICMS at the substrate temperature 725℃ recorded the value of T_C a little higher than 90K. Some other samples films that were produced on $LaAlO_3$ and $SrTiO_3$ showed T_C in the range of 85–90K. These results are well compared with T_C of $YBa_2Cu_3O_{7-d}$ crystals[14)] and considered good enough to further proceed to next procedures.

A four-probe multimeter unit constructed with a Nanovoltmeter and a current source was directly applied to the samples in order to

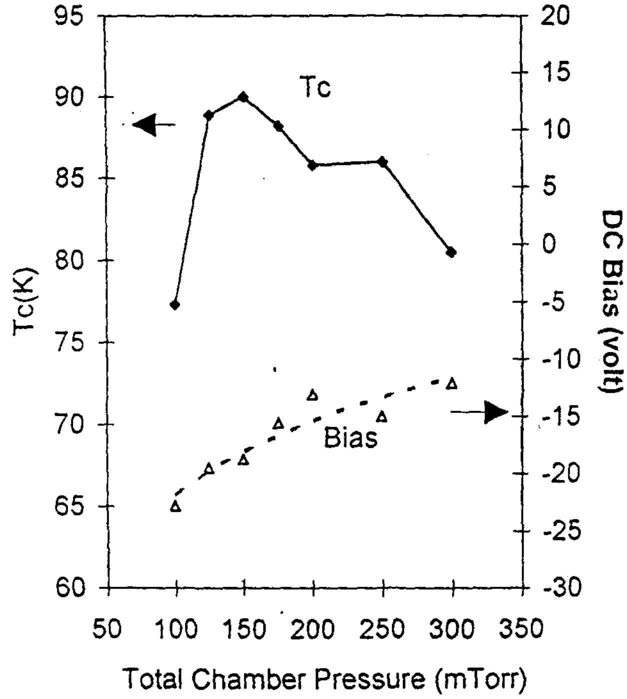

Fig. 3. Plot of T_C and DC bias vs. total chamber pressure for the samples processed at T_{sub}=770℃ and Ar/O_2 ratio=9.

measure the values of direct current flowing across the thin film samples at a fixed low temperature. At T=5K without magnetic influence, a calculation rendered the values of J_C being larger than 2×10^7A/㎠. And these samples were subjected to a temperature T=77K with H=0 Tesla, they showed the value of J_C larger than 1×10^6A/㎠. Crystallinity of the film samples was also investigated with an X-ray diffraction technique. As shown in Fig. 4, a film grown at 740℃ revealed that the 123 phase was formed incompletely. Meanwhile, others grown at 760-780℃ demonstrated their completeness through the orientation of {001} peaks in the XRD spectra (some silver peaks identified also were from the silver paste used for attaching the sample to the sample holder) which proves that the 123 grains were grown along the c-axis epitaxially (see Fig. 4). It has been concluded, therefore, thin $YBa_2Cu_3O_{7-d}$ films grown on MgO substrate showed good feasibility in reproduction, particularly for MgO possessing strong chemical stability and excellent dieletric property compared with others, which would be crucial in manufacturing electronic devices.

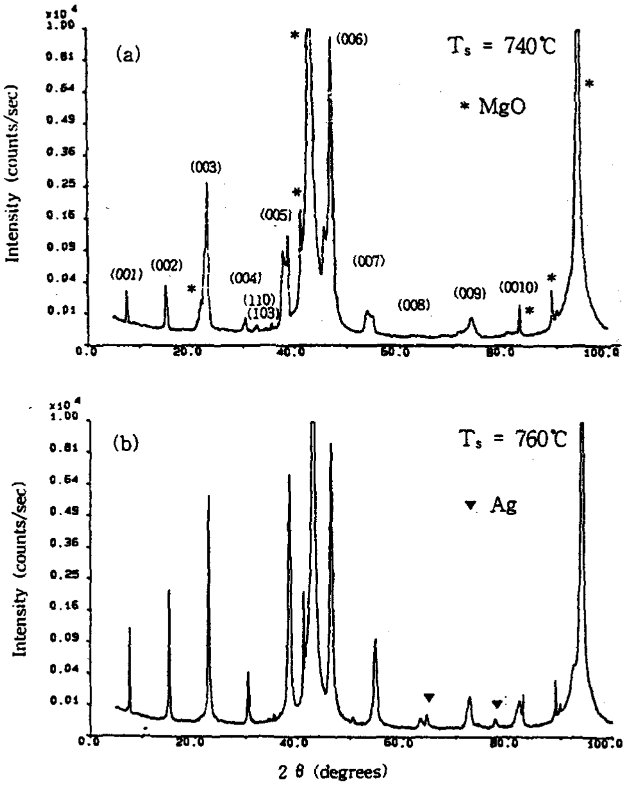

Fig. 4. X-ray diffraction patterns of the films deposited at (a) 740℃ and (b) 760℃ under the pressure of 200mTorr

Chemical Etching and Film characteristics

Nitric acid (2% solution) was too strong and fast to control the etch rate in the $YBa_2Cu_3O_{7-d}$ thin films. The etch rate was varied within 100-120 nm/sec and the etched surface turned out to be non-uniform. Both of phosphoric acid and EDTA solution, however, showed a lot better surface condition with the etch rate in the rage of 2 to 80nm/sec, depending on their concentrations. Under an optical microscopy, the etched samples showed some difference in dimmensions from the photomask pattern. This seemed to be caused by over-developing and etching undercut. And in the case of non-uniform chemical composition in a specimen due to the second phase particulates, the specimen surface showed some residues after etching. The films produced at 650℃ and below rendered nice etching, while those grown at 700℃ and above left some fine residues. The reason for this would be due to a reaction and/or a strong adhesion between YBCO film and its substrate at higher temperatures.

Fabricating visually good quality micro-bridges with the line width varying from 10 down to 2 microns, we found that the values of T_C and J_C for the $YBa_2Cu_3O_{7-d}$ samples decreased monotonically as the width of lines that were patterned through the etching process decreased. Specifically, the resistivity-temperature curves showed the decreasing values of T_C while the room temperature resistivities increased up to three times and there was little change in the thermal characteristics trend. We have found that the relation between T_C after etching, T_C(e), and line width (L) is interestingly common among various film samples⁽⁷⁾ possessing different T_C values although the absolute degradation amounts differ from each other. The degradation tendency became meaningful when the values of $T_C(e)$ were normalized.

Fig. 5 depicts the typical normalized data, a plot demonstrating the dependence of normalized temperature, N, on L. The graph seems revealing an exponential behavior, approaching to 1 as L increases sufficiently. Degradation owing to chemical etching process[6] is related with several background reasons: a) the undercutting phenomena via isotropic etching, b) the roughness of film surface, c) the surface reaction between $YBa_2Cu_3O_{7-d}$ material and water or chemical solution, and d) the non-uniformity of chemical composition in the thin film.

Estimation for $T_C(e)$

To estimate the values of $T_C(e)$ as a function of L keeping in mind a fundamental basis of the relation for the upper limit of N to be a unity, a formula is proposed here :

$$N=T_C(e)/T_C(b)=1-a/e^{1000\ bL} \qquad (Eq.\ 1)$$

where $T_C(b)$ is the value of T_C in the absolute scale before the etch process, a and b are the proper fitting constants, L is the line width in mm. In order to fix the constants a and b, Eq. 1 would be first rearranged as follows.

$$-\ln(1-N)=bL-\ln a \qquad (Eq.\ 2)$$

In Fig. 6, the values of $-\ln(1-N)$ for the typical T_C data obtained experimentally are shown against L, which presents a linear relationship. The best fitting straight line has been found to penetrate a point (0, 1.2) with a slope of 0.22 in the coordinate system. Therefore, the values of a and b woud be obviously exp(−1.2) and 0.22, respectively. As these values were introduced to Eq. 1, an exponential relation between N and L has been obtained as $N=1-1/\exp(220L+1.2)$ that has been shown as a curve (the broken line) in Fig. 5.

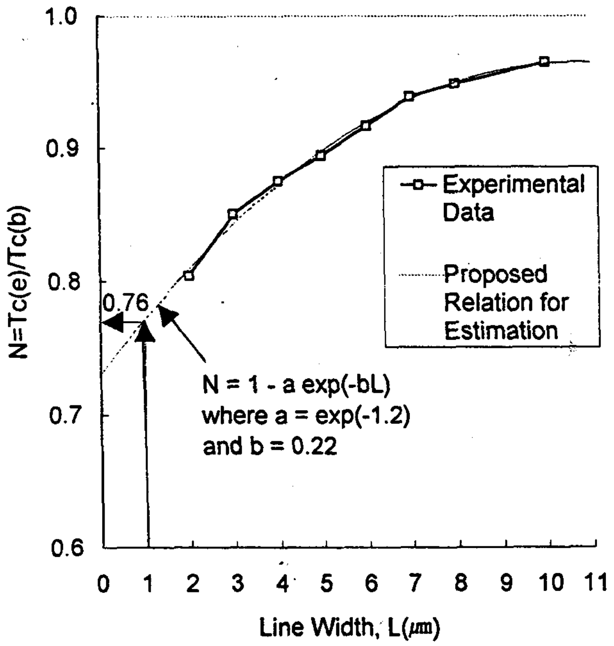

Fig. 5. Normalized values of the transition temperatures of etched specimens, $T_C(e)$ being devided by each corresponding T_C before etching, $T_C(b)$, which are plotted against the corresponding line widths.

As shown in Fig. 5, the estimated values have fit very well with the experimental data. Eq. 1 would have a great importance for the limitation of patternability due to photonic resolution limit as about 1 micron, in prediction of the $T_C(e)$ whether the thin film would yield a meaningful HTS device.

Applications of Results

Making use of this equation, one could predict the critical temperature of an 123-YBCO film degraded after chemical etching to pattern out a superconducting circuit line of any

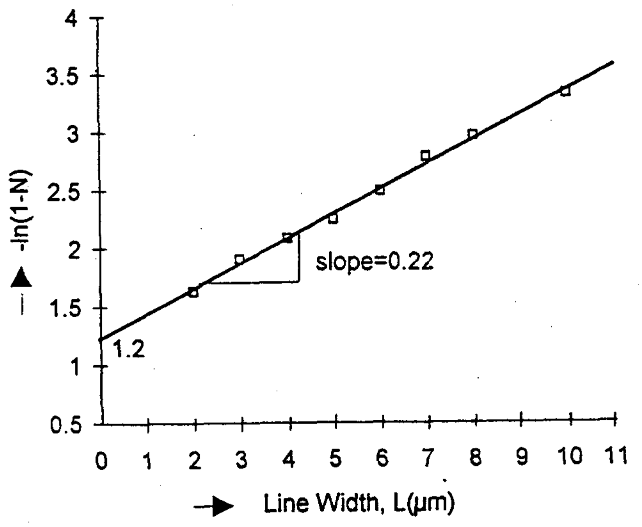

Fig. 6. An exponential relation between the normalized temperature and line width.

width. For this purpose, Fig. 5 could be utilized conveniently. For an example with a line width of 1 micron, the normalized temperature N is 0.76, i.e. $T_c(e)$ is predicted as 76% of $T_c(b)$. From the estimated values, we could decide the upper limits of the device operation temperature. This means that a microelectronic device with a $YBa_2Cu_3O_{7-d}$ film prepared through chemical etching process might be in a jeopardy at the liquid nitrogen temperature, but yet in good operation at the temperatures reasonably higher than the liquid helium temperature.

The data collected so far convinced us that grain boundary Josephson junctions utilizing this type of microbridges could be quite comfortably fabricated using the processes described here but to improve the operating temperature up to 77K, ion-milling method would be a reasonable choice, hopefully free of such degradation. This would lead us surely to a successful development of a SQUID as an active microelectronic device,[15] further a magnetometer and also a gradiometer, ever known as the ultimate fine magnetic sensor with resolutions of 10^{-14} Tesla, 10^{-18}V and 10^{-18} A, to even analyze the brain signals. The issue of commercialization of this technology, then, would lie on the question in quality of the $YBa_2Cu_3O_{7-d}$ films grown on MgO substrates and patterned with much less degradation in surface characteristics.[16]

4. CONCLUSIONS

Superconducting films of $YBa_2Cu_3O_{7-d}$ were synthesized on various substrates by using the methods of off-axis magnetron sputtering and annealing in-situ. The deposition results showed a good feasibility with the MgO substrate. The value of T_c higher than 90K was obtained for the sample films, along with the value of J_c measured with H=0 Tesla and T=77K being larger than 10^6A/㎠. The quality of thin films was good enough to build micro-electronic devices operating at the boiling temperatue of liquid nitrogen. Thin film etching experiments with a variety of etchants resulted that phosphoric acid and/or EDTA solution yielded a good surface condition and handlability. The sample films were examined before and after etching to reveal any changes. Data showed a tendency of degradation in T_c, specifically with the narrow line width. A simple relationship between $T_c(e)/T_c(b)$ and L has been proposed with a formula $T_c(e)/T_c(b) = 1 - a\ \exp(-1000\ bL)$ with $a = \exp(-1.2)$ and $b = 0.22$. This equation showed an exellent agreement with the experimetal data. So it was useful in predicting the upper limit of operation temperature for a superconducting device. These results of development activities have been a part of fundamental building blocks for the manufacturing technology of a SQUID magnetometer and for its optimization, thus would be considered as very useful for the future work.

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