

Aging Effect of $\text{YBa}_2\text{Cu}_3\text{O}_x$ Targets in RF Magnetron Sputtering

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Abstract

The aging effect of $\text{YBa}_2\text{Cu}_3\text{O}_x$ oxide targets in rf magnetron sputtering was studied. Film composition, target bias voltage, deposition rate and emission spectra of plasma resulting from sputtering of a newly fabricated target were examined as a function of sputtering time. The composition of thin films deposited on MgO (100) single crystals was initially off-stoichiometric and stable compositions were achieved after 40 h of sputtering. The target bias voltage decreased for the first 4 h due to desorption of adsorbed water vapor in the sputtering chamber and increased to a steady-state after 40 h of sputtering. The increase of target bias voltage after 10 h is due to decrease of oxygen from the target surface. This was confirmed by the decrease of emission intensity from oxygen. With decrease of oxygen from the surface, sputtering yields of Y, Ba and Cu increase and the deposition rate increases. The sputtering yields of Y and Ba are more sensitive to the oxygen content than that of Cu. The emission intensity of Y, Ba and Cu increases with the sputtering time due to the increase of sputtering yields and probability of being excited by the discharge electrons.

1. Introduction

Sputter deposition is a popular method of fabricating thin films. By bombarding a target with fast positive ions such as Ar^+ , target atoms are removed from the target and deposited on a substrate. It has revealed as the one of the most valuable techniques to deposit thin films of high-temperature superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ oxide. Although films can be routinely deposited by this method, there remains problems to obtain high-quality films. One of the major problems encountered in a single target sputter process is poor stoichiometry in as-deposited films. Two major contributors to poor stoichiometry are aging of the target¹⁻²⁾ and sensitivity to process variables³⁻⁶⁾.

Selinder *et al.*¹⁾ had grown $\text{YBa}_2\text{Cu}_3\text{O}_x$ thin films from stoichiometric oxide targets using dc magnetron sputtering. Initially, the film composition was strongly off-stoichiometric and deposition rate very low (0.05 nm/s). However, after extensive presputtering, stoichiometric films, with respect to the metal content, were deposited at a rate of 0.25 nm/s. They assigned that the long presputtering time of 20-30 h needed was due to a slowly changing oxygen content on the target surface. Because of the bad thermal conductivity of the target materials, the impinging ions gave rise to an increase in the temperature of the target. At these relatively high temperatures, oxygen bulk diffusion was rapid. Thus, when sputtering from a composite oxide target in pure Ar discharges, the oxygen depletion of the target surface did not reach a steady-state value until a large region of the target had been depleted

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of oxygen. This was confirmed by sputtering from a target that prior to installation in the sputtering source was annealed in an Ar atmosphere for 6 h at 800°C. The time to obtain steady state conditions was reduced from 20–30 h to ~8 h for this target.

Klein and Yen²⁾ reported that the plasma emission spectra resulting from rf sputtering of $\text{YBa}_2\text{Cu}_3\text{O}_x$ targets were a function of sputtering time. They observed that the emission spectra from a newly fabricated target exhibited a slow first-order transient response in seeking equilibrium with the rf plasma, but the transient response of a previously sputtered target was also first order but had a much shorter time constant.

It is necessary to know the complete understanding of the microscopic details of the methods by which high-quality superconducting thin films are deposited. To accomplish the understanding of the sputter deposition and eventually control this process, real time diagnostics for sputter deposition are needed. One method is optical emission spectroscopy. When positive ions strike a solid target, it may cause ejection of target atoms as ions or as ground-state or excited-state neutral atoms. The presence of excited atoms and molecules in the stream of particles leaving the target directed toward the substrate provides a convenient diagnostic tool. With a relatively simple optical measuring system, the identity of some of the particles leaving the target may be determined. Changes in sputtering parameters such as argon and oxygen partial pressures, etc., are reflected in changes in the optical output from species near the target surface. Although this measurement method is relatively easy to implement, it has some limitations. Optical emission measurements access only a small fraction of the particles ejected from the target; not all species from the target will be excited, and for a given species, only a small percentage of the particles will be in an excited state. The advantages of this technique outweigh the disadvantages by providing an *in situ*, non-perturbing method of monitoring the sputter deposition process.

In this paper, we study the film composition, the target bias voltage, the deposition rate and the spectroscopic study of the emission from plasma induced by rf sputtering of a newly fabricated $\text{YBa}_2\text{Cu}_3\text{O}_x$ target in order to see the aging effect of the target.

2. Experimental Setup

Stoichiometric composite $\text{YBa}_2\text{Cu}_3\text{O}_x$ targets were used in these experiments. Commercial $\text{YBa}_2\text{Cu}_3\text{O}_x$ powder was calcined at 900°C, pressed to form a 2-inch-diameter target and sintered at 950°C. The target was bonded to a magnetron source (LESKER MODEL TRS-002C) using an indium sheet. Sputtering was done in a pure Ar atmosphere. Ar gas pressure in a deposition chamber was fixed to 10 Pa. Ar gas was introduced in the sputter chamber through a gas flow controller (MKS TYPE 246). The sputtering pressure was monitored both by Schultz and Pirani gauges and held constant using the gas flow controller. A rf (13.56 MHz) power of 50 W was supplied to the target. To measure a dc component of the target voltage, electrical resistances of 1 M Ω and 10 k Ω were connected in series to the target and a capacitor of 0.01 μF was connected in parallel to the electrical resistance of 10 k Ω . Voltage of the 10 k Ω resistance was measured by a digital voltmeter and multiplied by

a factor of 101 to obtain the target bias voltage.

Thin films for compositional and thickness analysis were deposited on MgO single crystals $10 \times 5 \times 0.5 \text{ mm}^3$ in size. The substrate holder was held at ground potential, and the substrate were not intentionally heated to obtain a sticking coefficient close to unity for all atoms. All films described in this letter were analyzed in as-deposited condition without any post-annealing. This should give nearly identical composition of the films as compared with the flux of sputtered atoms from the target. Energy dispersive x-ray spectroscopy (EDS) was carried out to determine the metallic composition of the as-deposited films. Stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_x$ bulk samples were used as elemental standards when calibrating the EDS analyses. The deposition rate was measured by a quartz-crystal sensor (INFICON MODEL XTM/2). The sensor was calibrated by a multiple beam interferometer (MIZOJIRI OPTICAL MODEL BM-4).

When the plasma started, the bright region was ring shaped. The optical emission from this region was analyzed. Light emitted by the plasma passed through a quartz window and an optical filter (to eliminate second-order diffracted lights), was chopped by a light chopper and focused on an entrance slit of a 50-cm monochromator (SPEX MODEL 1870) by a quartz lens. Spectral resolution of the monochromator was 0.048 nm. Signals detected by a photomultiplier (HAMAMATU R928) were amplified using a lock-in amplifier. The lock-in amplifier and the monochromator were controlled by a computer.

3. Experimental Results and Discussion

A newly fabricated $\text{YBa}_2\text{Cu}_3\text{O}_x$ target was bonded to a magnetron source. Sputtering was done without interruption for 70 h in a pure Ar atmosphere. Figure 1 shows the film composition as a function of sputtering time. In the Figure, open circles represent Y, filled circles Ba, open triangles Cu, respectively. Stoichiometric compositions (Y: 16.7%, Ba: 33.3%, Cu: 50.0%) are indicated by dashed lines. The film composition is initially off-stoichiometric (Y: 21%, Ba: 20%, Cu: 59%), with Ba being deficient, and Cu and Y in excess. However, after 40 h of sputtering, stable conditions (Y: 22%, Ba: 32%, Cu: 46%) are achieved. An initial off-stoichiometric composition is normal when sputtering is done from an alloy or compound target. A layer of altered composition is formed on the target surface if the sputtering yields of the constituent atoms are different. The time needed to stabilize the film composition is dependent on factors such as differences in sputtering yields, ion energy, and ion flux, but usually only in the range of a few minutes⁷⁾. To see the surface state of the target, target bias voltage, deposition rate and emission spectra were measured.

Figure 2 shows the target bias voltage as a function of sputtering time. The target bias voltage is about -100 V when the sputtering starts, soon decreases to about -48 V at 4 h and increases gradually after 10 h. At the sputtering time of about 20 h, the target voltage increases rapidly to about -130 V and soon decreases. The target voltage still increases to about -80 V at 40 h. The steady-state condition is reached first after 40 h of sputtering. The drop of the target voltage from -100 V to -48 V at the start of sputtering may be due

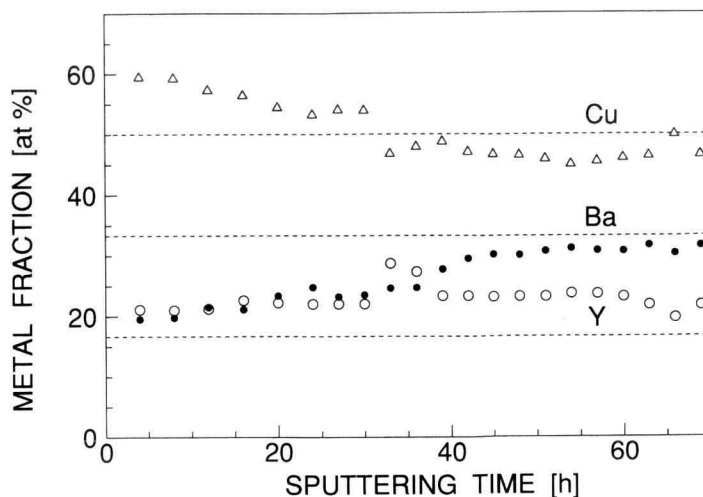


Fig. 1 Composition of the as-deposited films as a function of sputtering time. Open circles represent Y, filled circles Ba, open triangles Cu, respectively. Stoichiometric compositions (Y : 16.7%, Ba : 33.3%, Cu : 50.0%) are indicated by dashed lines.

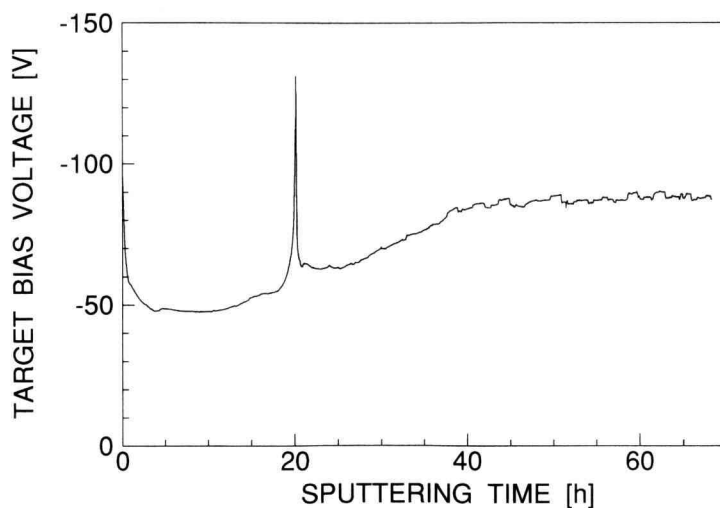


Fig. 2 Target bias voltage as a function of sputtering time.

to the desorption of adsorbed water vapor in the sputtering chamber. Specific lines of OH according to the reaction $\text{H}_2\text{O} + e^- \rightarrow \text{OH} + \text{H} + e^-$ were observed in the wavelength range of 280–320 nm⁸⁾. Figure 3 shows emission spectra of OH in the wavelength region of 309–327 nm. In this case, the target has been already sputtered for 70 h and was exposed to air. Emission spectra at the sputtering time of about 1.5 h and 5 h are shown in Fig. 3 (a) and (b), respectively. Fine structures due to OH observed in the wavelength range of 309–327 nm at

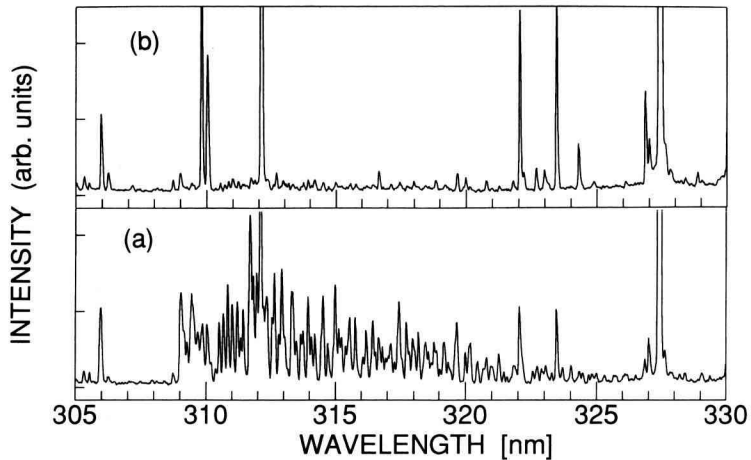


Fig. 3 Emission spectra by the target which had been already sputtered for 70 h and exposed to air. (a) at sputtering time of about 1.5 h. (b) at sputtering time of about 5 h.

the sputtering time of 1.5 h have disappeared at the sputtering time of 5 h. On the other hand, the increase of the target voltage after 10 h may be due to variations in the oxygen content of the target surface.

Figure 4 shows the deposition rate measured by a quartz-crystal sensor as a function of sputtering time. In contrast to the target bias voltage, the deposition rate increases at the start of sputtering. Except for the first 0.5 h, the time dependence of the deposition rate is similar to that of the target bias voltage. From Figs. 2 and 4, the deposition rate is proportional to the target bias voltage. The number of atoms such as Y, Ba and Cu ejected

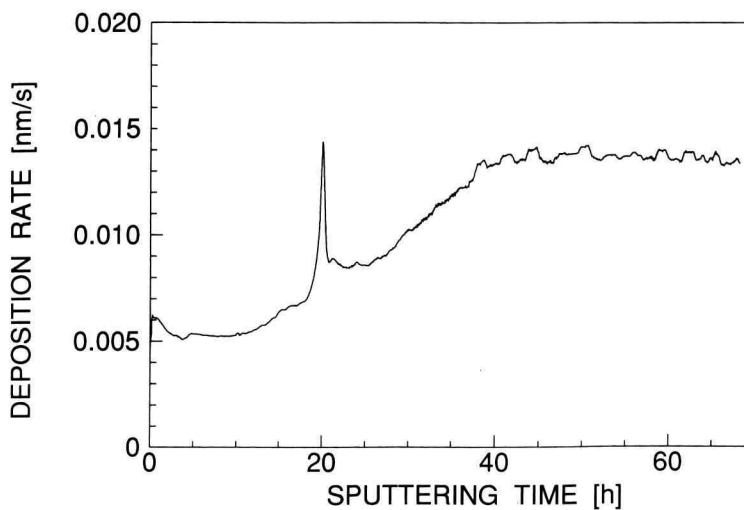


Fig. 4 Deposition rate as a function of sputtering time.

Table I. Atomic and ionic emission lines which are examined.

Emitting species	Emission line (in nm)		
Ar I	419.832	420.068	425.936
Ar II	427.755	458.993	460.960
Y I	410.238	414.284	464.370
Y II	371.029	377.433	
Ba I	553.555	577.767	582.630
Ba II	413.066	455.404	493.409
Cu I	324.754	327.396	333.784
O I	777.193	777.414	777.543

from the target is expected to be proportional to the target bias voltage.

In order to investigate variations of the oxygen content at the target surface and to monitor the stoichiometry of the deposited films, we measured emission spectra of plasma generated by rf magnetron sputtering. A spectroscopic analysis of plasma in the wavelength region from 300 to 870 nm reveals many emission lines due to Ar, Ba, Cu, O and Y. The observed emission lines are identified according to standard tables of spectral lines⁹⁻¹⁰.

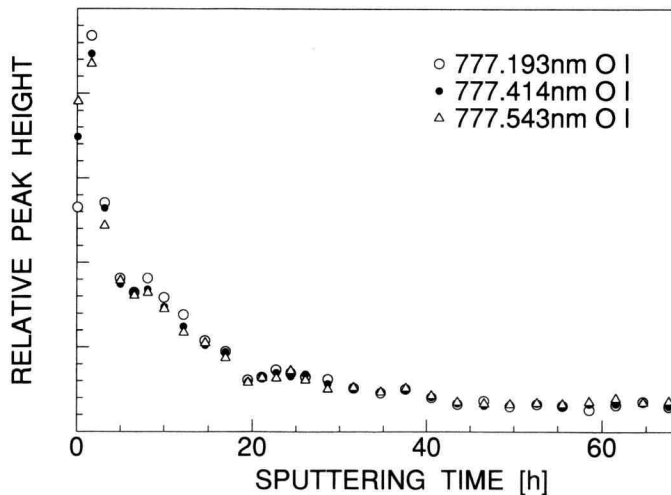


Fig. 5 Relative peak heights of O I as a function of sputtering time. Open circles represent 777.193 nm O I, filled circles 777.414 nm O I, open triangles 777.543 nm O I, respectively.

Emission lines whose time dependence are examined are listed in Table I. In the Table, the numerals I or II after the elements indicate that the lines have been assigned to a neutral atom (I) or to a singly ionized atom (II)⁹. These lines are the most intense lines and do not overlap the other lines. The dependence of these peak heights on sputtering time is measured.

Figure 5 shows relative peak heights of O I as a function of sputtering time. In the Figure, open circles represent 777.193 nm O I, filled circles 777.414 nm O I, open triangles 777.543 nm O I, respectively. When the sputtering starts, relative peak heights increase and peaked at 1 h, and decrease almost monotonously after this. After 40 h of sputtering, peak heights of O I reduce to 1/12 and become steady states. By depletion of oxygen from the target surface, electrons in the plasma move to the target and bias the target voltage to negative value. The reason that emission of O I do not vanish at this steady state is that the bombardment of Ar^+ ions gives rise to the increase in the temperature of the target, and at these relatively high temperatures, oxygen bulk diffusion is rapid¹¹. Thus, when sputtering from an oxide target in pure Ar discharges, the release of oxygen from the target surface did not vanish until a whole region of the target had depleted its oxygen. At sputtering time of about 20 h where the target bias voltage has a sharp peak, there is a little dip in the emission of O I. At this dip, the temperature of target is not at the moment high enough to diffuse oxygen to compensate the sudden decrease of oxygen at the target surface. But, the temperature of target soon increases by the bombardment of Ar ions accelerated by the increased target voltage and diffusion of oxygen to the target surface reduces the target bias voltage.

Figure 6 shows relative peak heights of Y as a function of sputtering time. In the

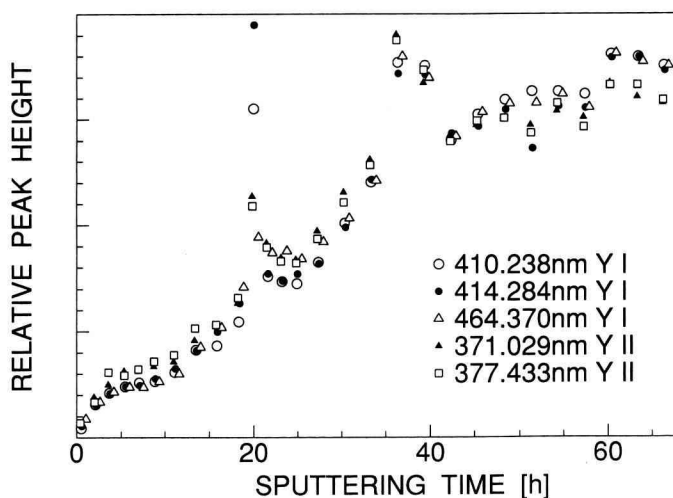


Fig. 6 Relative peak heights of Y as a function of sputtering time. Open circles represent 410.238 nm Y I, filled circles 414.284 nm Y I, open triangles 464.370 nm Y I, filled triangles 371.029 nm Y II, open squares 377.433 nm Y II, respectively.

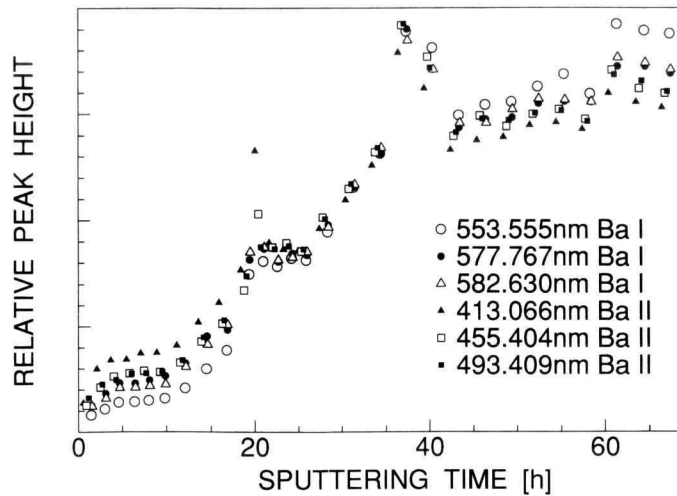


Fig. 7 Relative peak heights of Ba as a function of sputtering time. Open circles represent 553.555 nm Ba I, filled circles 577.767 nm Ba I, open triangles 582.630 nm Ba I, filled triangles 413.066 nm Ba II, open squares 455.404 nm Ba II, filled squares 493.409 nm Ba II, respectively.

Figure, open circles represent 410.238 nm Y I, filled circles 414.284 nm Y I, open triangles 464.370 nm Y I, filled triangles 371.029 nm Y II, open squares 377.433 nm Y II, respectively. Figure 7 shows relative peak heights of Ba as a function of sputtering time. In the Figure, open circles represent 553.555 nm Ba I, filled circles 577.767 nm Ba I, open triangles 582.630 nm Ba I, filled triangles 413.066 nm Ba II, open squares 455.404 nm Ba II, filled squares 493.409 nm Ba II, respectively. The time dependence of peak heights of Y and Ba has a similar

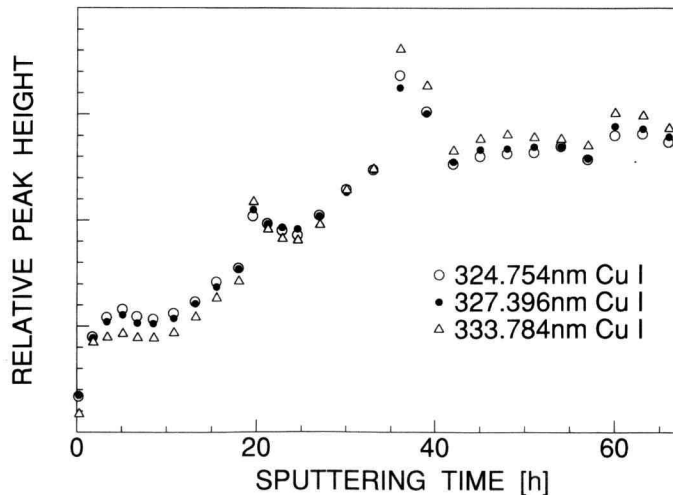


Fig. 8 Relative peak heights of Cu as a function of sputtering time. Open circles represent 324.754 nm Cu I, filled circles 327.396 nm Cu I, open triangles 333.784 nm Cu I, respectively.

behavior. At the start of sputtering, relative peak heights of Y and Ba are quite small, but increase approximately in proportion to the sputtering time, and increase slowly even after 40 h when the target bias voltage becomes the steady-state value.

Figure 8 shows relative peak heights of Cu as a function of sputtering time. In the Figure, open circles represent 324.754 nm Cu I, filled circles 327.396 nm Cu I, open triangles 333.784 nm Cu I, respectively. The time dependence of Cu I has a different behavior from that of Y and Ba. The relative peak heights of Cu I increase rapidly at the start of sputtering, have a little dip at 8 h and increase approximately in proportion to the sputtering time, and become a steady state at 40 h.

To monitor the ratio of Y, Ba and Cu atoms sputtered from the target by optical emission spectroscopy, we calculate peak height ratios of emission lines of Ba and Cu to Y. Figure 9 shows peak height ratio of Ba to 410.238 nm Y I as a function of sputtering time. Peak height ratios of 553.55 nm, 577.767 nm and 582.630 nm Ba I to 410.238 nm Y I are almost independent of sputtering time. However, peak height ratios of 413.066 nm, 455.404 nm and 493.409 nm Ba II to 410.238 nm Y I decrease at the start of sputtering, and become steady values at sputtering time of 10 h. The difference of the time dependence between Ba I and Ba II at the start of sputtering may be due to the desorption of adsorbed water vapor in the sputtering chamber. By the existence of water vapor desorbed from the sputter chamber, the discharge electrons excite more Ba ions than Ba neutral atoms. The compositional ratio of Ba to Y increases from 1 to 1.5 with sputtering time of 40 h, but the time dependence of the peak height ratio obtained by emission of Ba to Y is different from line to line and quantitative discussion is difficult.

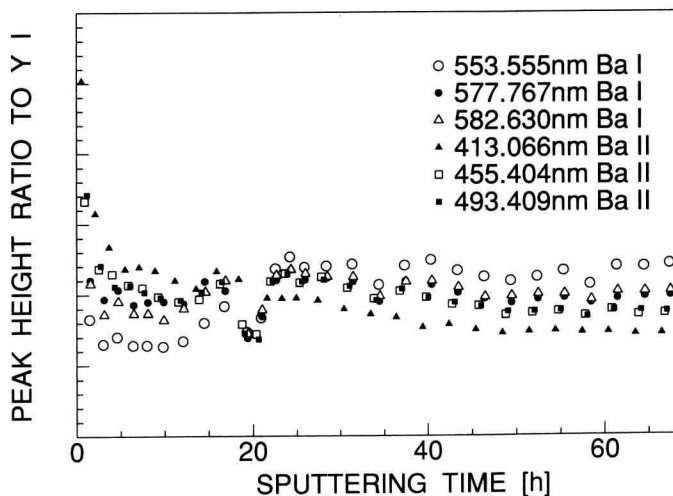


Fig. 9 Peak height ratio of Ba to 410.238 nm Y I as a function of sputtering time. Open circles represent 553.555 nm Ba I, filled circles 577.767 nm Ba I, open triangles 582.630 nm Ba I, filled triangles 413.066 nm Ba II, open squares 455.404 nm Ba II, filled squares 493.409 nm Ba II, respectively.

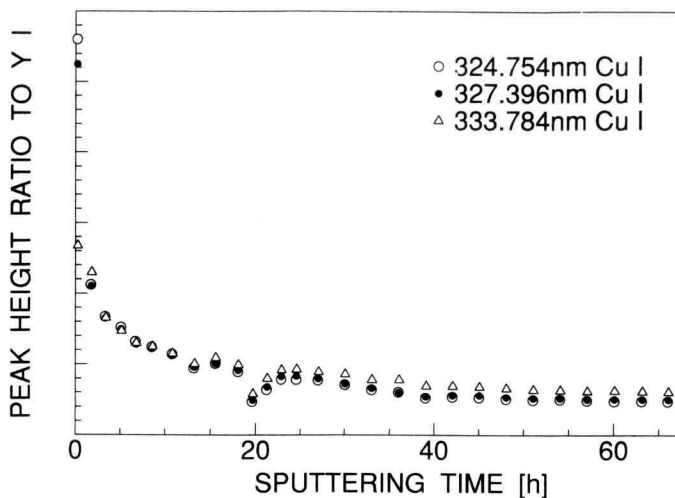


Fig. 10 Peak height ratio of Cu to 410.238 nm Y I as a function of sputtering time. Open circles represent 324.754 nm Cu I, filled circles 327.396 nm Cu I, open triangles 333.784 nm Cu I, respectively.

Figure 10 shows peak height ratio of Cu to 410.238 nm Y I as a function of sputtering time. The peak height ratios of Cu I to Y I decrease to about 1/10 for sputtering time of 40 h. This result agrees qualitatively with the time dependence of the composition of the deposited films. As the compositional ratio of Cu to Y decreases from 3 to 2 with sputtering time of 40 h, the time dependence of peak height ratio obtained by emission is exaggerated.

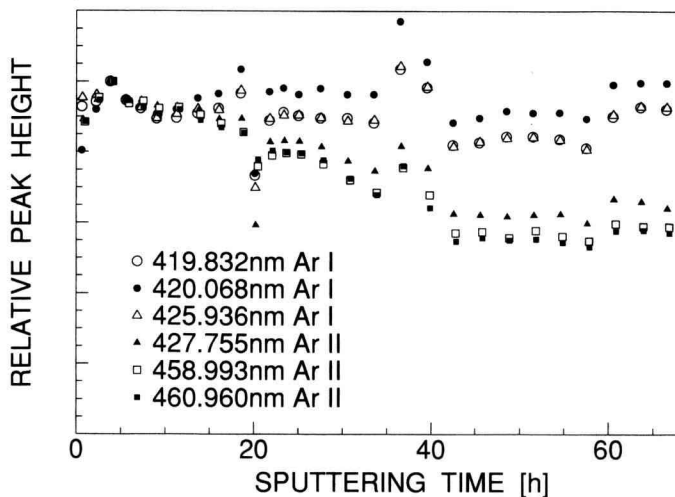


Fig. 11 Relative peak heights of Ar as a function of sputtering time. Open circles represent 419.832 nm Ar I, filled circles 420.068 nm Ar I, open triangles 425.936 nm Ar I, filled triangles 427.755 nm Ar II, open squares 458.993 nm Ar II, filled squares 460.960 nm Ar II, respectively.

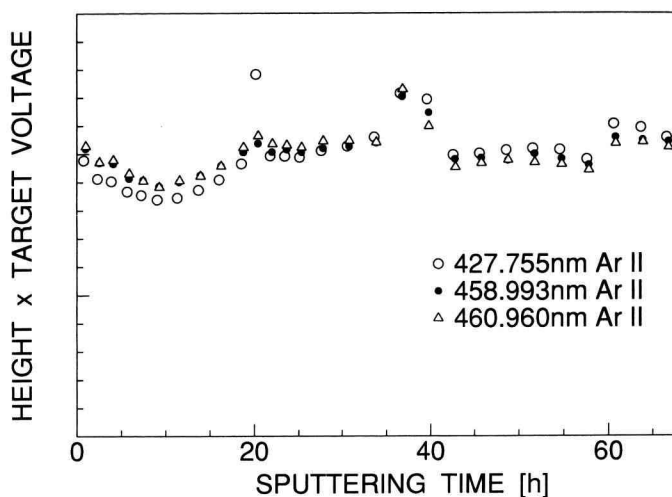


Fig. 12 Peak heights of emission lines multiplied by the target bias voltage as a function of sputtering time. Open circles represent 427.755 nm Ar II, filled circles 458.993 nm Ar II, open triangles 460.960 nm Ar II, respectively.

Figure 11 shows the relative peak heights of Ar as a function of sputtering time. In the Figure, open circles represent 419.832 nm Ar I, filled circles 420.068 nm Ar I, open triangles 425.936 nm Ar I, filled triangles 427.755 nm Ar II, open squares 458.993 nm Ar II, filled squares 460.960 nm Ar II, respectively. Peak heights of emission from Ar I are almost independent on the sputtering time. As the sputtering is done in the constant Ar pressure, intensity of emission from neutral Ar atoms will not change with the sputtering time. On the other hand, peak heights of emission from Ar II decrease slowly and the steady-state condition is reached first after 40 h of sputtering. As peak heights of emission by Ar II, namely Ar^+ ions are expected to be proportional to a current going through the target, peak heights of emission lines of Ar II multiplied by the target bias voltage will be proportional to an electric power supplied to the target. Figure 12 shows peak heights of emission lines of Ar II multiplied by the target bias voltage as a function of sputtering time. In the Figure, open circles represent 427.755 nm Ar II, filled circles 458.993 nm Ar II, open triangles 460.960 nm Ar II, respectively. These products are almost independent on the sputtering time. The decrease of the peak heights of emission from Ar II with sputtering time corresponds to the decrease of the target current. Although the number of Ar^+ ions impinging to the target decreases with sputtering time, the peak heights of emission lines by Y, Ba and Cu increase from ten to forty times. This is due to the increase of sputtering yields of Y, Ba and Cu by depletion of oxygen at the target surface. The increase of the sputtering yields of Y and Ba is larger than that of Cu. Also oxygen concentration in the plasma decreases, the probability for Y, Ba and Cu of being excited by the discharge electrons increases. The emission intensity of Y, Ba and Cu increases with the sputtering time due to the increase of sputtering yields and probability of being excited by the discharge electrons.

4. Conclusion

We have studied the aging effect of $\text{YBa}_2\text{Cu}_3\text{O}_x$ target in the rf magnetron sputtering. The film composition, the target bias voltage, the deposition rate and the emission spectra resulting from sputtering of a newly fabricated target were measured as a function of sputtering time. The composition of the films deposited on MgO (100) single crystals was initially off-stoichiometric, with Ba being deficient, and Cu and Y in excess. After 40 h of sputtering, stable compositions were achieved. The target bias voltage decreased for the first 4 h, increased after 10 h, had a sharp peak at 20 h, and the steady-state was reached after 40 h of sputtering. The decrease of the target bias voltage for the first 4 h is due to the desorption of adsorbed water vapor in the sputtering chamber, and the increase of target bias voltage is due to removal of oxygen from the target surface. This was confirmed by the decrease of emission intensity from oxygen. As oxygen at the target surface decreases, sputtering yields of Y, Ba and Cu increases and the deposition rate increases. The sputtering yields of Y and Ba are more sensitive to the oxygen content of the target than that of Cu. Also oxygen concentration in the plasma decreases, the probability for Y, Ba and Cu of being excited by the discharge electrons increases. The emission intensity of Y, Ba and Cu increases with the sputtering time due to the increase of sputtering yields and probability of being excited by the discharge electrons.

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