

# Sputtered Species from Cu and $\text{YBa}_2\text{Cu}_3\text{O}_x$ Targets Studied by Quadrupole Mass Spectrometer

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## Abstract

In order to clarify the sputtered species from a target, a quadrupole mass spectrometer system evacuated differentially was developed. A copper metal target was sputtered to test this system. The system detected  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  of copper isotopes in mass spectra. The observed ratio of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  was 7:3, which was close to the value of 69:31, the natural abundance of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ . This result showed that the system could detect Cu atoms sputtered from Cu metal target. In the case of an  $\text{YBa}_2\text{Cu}_3\text{O}_x$  oxide target, the system detected Y, Ba and Cu signals. However, the observed signals of Ba or Cu isotopes were almost the same intensities, contrary to the expected values of the natural abundance of Ba or Cu. The observed signal was not due to sputtered species from the oxide target.

**Key Words:** high-temperature superconductor, sputter deposition, thin films,  
quadrupole mass spectrometer

## 1. Introduction

Sputter deposition is a popular method of depositing thin films. By bombarding a target with accelerated ions such as argon ions, target atoms are removed from the target and deposited on a substrate. It has been revealed as the one of the most valuable techniques to deposit thin films of high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_x$  oxide. Although films can be routinely deposited by this method, it remains difficult to obtain high-quality films. One of the major problems encountered in a composite target sputter process is poor stoichiometry in as-deposited films. Major contributors to the

poor stoichiometry are the sensitivity to sputtering parameters such as argon and oxygen partial pressures<sup>1-2)</sup>, substrate temperatures<sup>3)</sup>, a position of substrate<sup>4-5)</sup>, and aging effect of the target<sup>6)</sup>.

As sputter yield is different for each atom, the composition of the deposited films is different from that of the target at the beginning of the sputtering. By the continuous sputtering of the target, the composition of the deposited films becomes similar to that of the target. The presputtering time needed is typically several minutes for a metal target, but a few hours for an oxide target<sup>6)</sup>.

It is necessary to know the complete understanding of the microscopic details of the methods by which high-quality superconducting films are deposited. To accomplish the understanding of the sputter deposition and eventually control this process, real time diagnostics for sputtering are needed. One method is the use of a quadrupole mass spectrometer (QMS)<sup>7)</sup>. Sputtered species from the target can be analyzed directly by using QMS under various sputtering conditions. The disadvantage of QMS is that the operating pressure of QMS is much lower than that of the sputtering chamber and differential evacuation is needed.

In this paper, in order to clarify the sputtering process, a QMS system evacuated differentially in two stages is developed. To test this QMS system, a copper metal target is sputtered. QMS system detects sputtered copper atoms from the target. Also an  $\text{YBa}_2\text{Cu}_3\text{O}_x$  target is sputtered and the detection of sputtered species from the target is tried by this QMS system.

## 2. Experimental

Figure 1 shows a schematic view of the apparatus for sputtering, used in this work. This apparatus consisted of a sputtering chamber equipped with a diffusion pump system, a magnetron source and a quadrupole mass spectrometer. Copper metal and stoichiometric composite  $\text{YBa}_2\text{Cu}_3\text{O}_x$  targets were used in this experiment.

Commercial  $\text{YBa}_2\text{Cu}_3\text{O}_x$  powder was calcined at  $900^\circ\text{C}$ , pressed to form a disk of 50 mm in

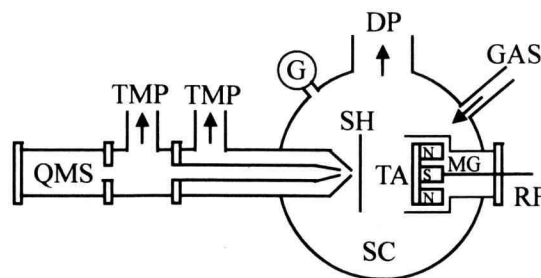


Fig. 1 A schematic view of an RF magnetron sputtering system equipped with a quadrupole mass spectrometer. (DP) diffusion pump, (G) ion gauge, (GAS) inlet of Ar and  $\text{O}_2$  gases, (MG) magnetron sputter source, (QMS) quadrupole mass spectrometer, (RF) RF power input, (SC) sputtering chamber, (SH) shutter, (TA) target, (TMP) turbomolecular pump.

diameter and 5 mm in thickness, and sintered at 950°C. The fabricated YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> target was held to the magnetron source (LESKER MODEL TRS-002C) using an indium sheet.

Sputtering was done in pure Ar atmosphere for the copper target, and in 80 % Ar / 20 % O<sub>2</sub> atmosphere for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> oxide target, respectively. A gas pressure in a sputtering chamber was fixed to 5.0 Pa. Ar and O<sub>2</sub> gases were introduced in the sputter chamber through gas flow controllers (MKS TYPE 246). The sputtering pressure was monitored both by Schulz and Pirani gauges and held constant using the gas flow controllers.

An RF power supply (KYOSAN MODEL RFK10) of 13.56 MHz was used. A quartz deposition monitor (INFICON MODEL XTM/2) was used for monitoring sputtered quantity. The change of the resonance frequency of the quartz sensor was proportional to the quantity attached to the sensor.

The quadrupole mass spectrometer (QMS) with a channeltron (ANELVA MODEL M-QA200TS) was used to get information about species sputtered from the target. As the QMS had to be operated under about 10<sup>-4</sup> Pa, a 50-cm-long double-layered guidance pipe with two orifices of 0.5 mm in diameter was attached to the QMS. The guidance pipe was evacuated differentially down first to about 10<sup>-2</sup> Pa, and second to about 10<sup>-4</sup> Pa by two turbomolecular pumps. The distance from the orifice to the target was 32 mm. A shutter located at the orifice was opened and closed at intervals of 150 s, to subtract the background signal from the QMS output current. The differences of QMS output signal were assigned due to the component of the species sputtered from the target.

### 3. Experimental Results and Discussion

#### 3.1 Copper Target

Figure 2 shows typical mass spectra observed by this QMS system in the range of mass number from 60 to 70, when a copper target is sputtered at RF input power of 100 W in 5 Pa pure Ar atmosphere. A solid line represents the mass spectrum when the shutter is opened, while a dotted line represents when the shutter is closed. In the Figure, labels of <sup>63</sup>Cu and <sup>65</sup>Cu represent isotopes of copper.

Figure 3 shows the typical QMS output current of <sup>63</sup>Cu as a function of a sputtering time at RF input power of 100W in 5 Pa pure Ar atmosphere. Open circles represent the observed values. As the shutter is opened and closed at the interval of 150 s, the QMS current changes simultaneously. This result shows that the QMS output current is noisy and has large background. A solid line represents the least-square-fitting curve. The step heights when the shutter is opened or closed are assigned to the QMS signals due to <sup>63</sup>Cu species sputtered from the target.

Figure 4 shows the averaged step height of QMS current as a function of RF input power in 5 Pa pure Ar atmospheres. Open and filled circles represent to those of <sup>63</sup>Cu and <sup>65</sup>Cu, respectively.

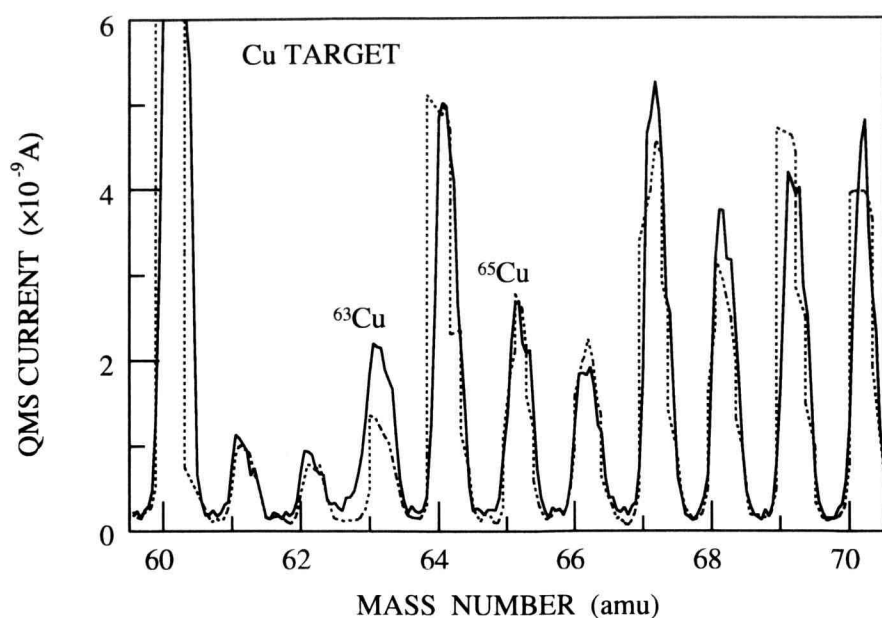


Fig. 2 Mass spectra of a copper target sputtered at RF input power of 100 W in 5 Pa pure Ar atmosphere. A solid line represents the spectrum when the shutter is open, while a dotted line represents when the shutter is closed. In the Figure, labels of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  represent isotopes of copper.

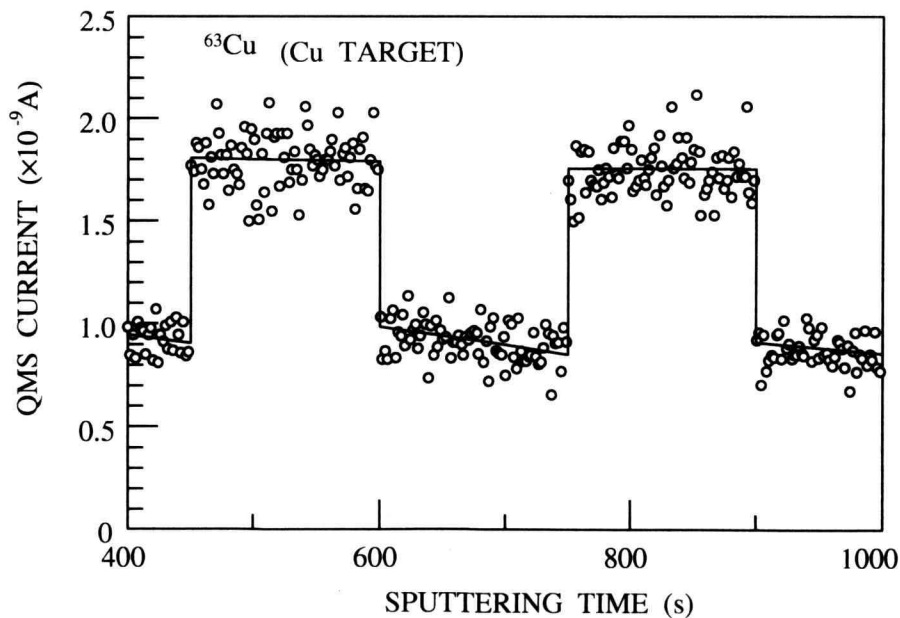


Fig. 3 QMS output current of  $^{63}\text{Cu}$  as a function of a sputtering time for a copper target sputtered by RF input power of 100 W in 5 Pa pure Ar atmosphere. Open circles represent the observed values, and a solid line represents the least-square-fitting curve.

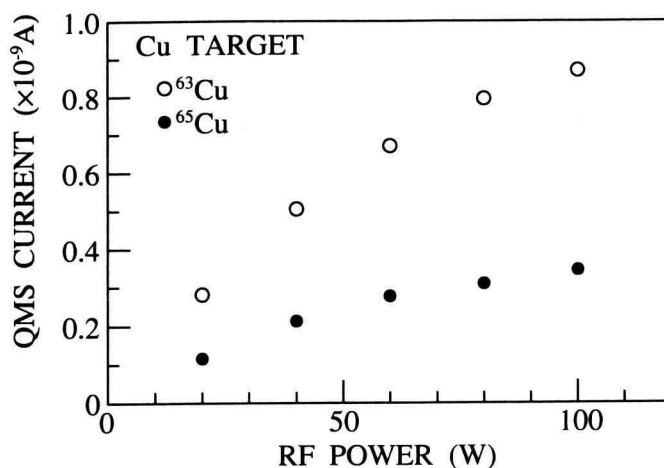


Fig. 4 QMS output current as a function of RF input power for a copper target sputtered in 5 Pa pure Ar atmosphere. Open and filled circles represent <sup>63</sup>Cu and <sup>65</sup>Cu, respectively.

QMS currents of <sup>63</sup>Cu and <sup>65</sup>Cu increase almost linearly with the RF power of the target. The averaged ratio of <sup>63</sup>Cu and to <sup>65</sup>Cu is about 7:3. The natural abundance of copper isotopes of <sup>63</sup>Cu and <sup>65</sup>Cu is 69:31. The ratio of <sup>63</sup>Cu and to <sup>65</sup>Cu observed by this QMS system is quite close to the natural abundance of <sup>63</sup>Cu and to <sup>65</sup>Cu.

To compare with this QMS system, a quartz sensor is positioned in the front of the target, instead of QMS system. Figure 5 shows the deposition rate of copper observed by the quartz deposition

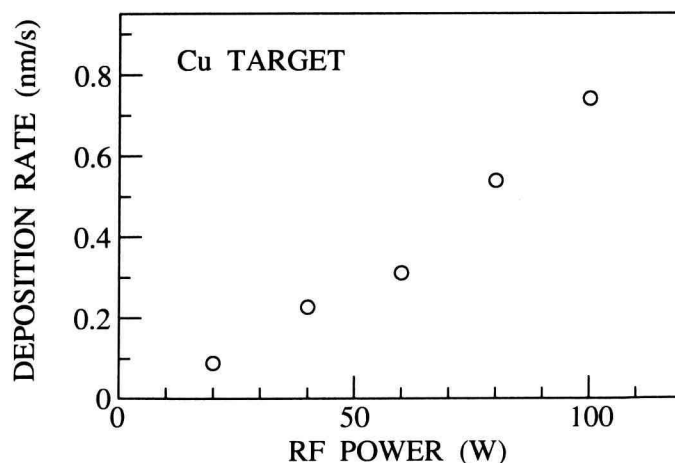


Fig. 5 Deposition rate observed by a quartz deposition monitor as a function of RF input power for a copper target sputtered in 5 Pa pure Ar atmosphere.

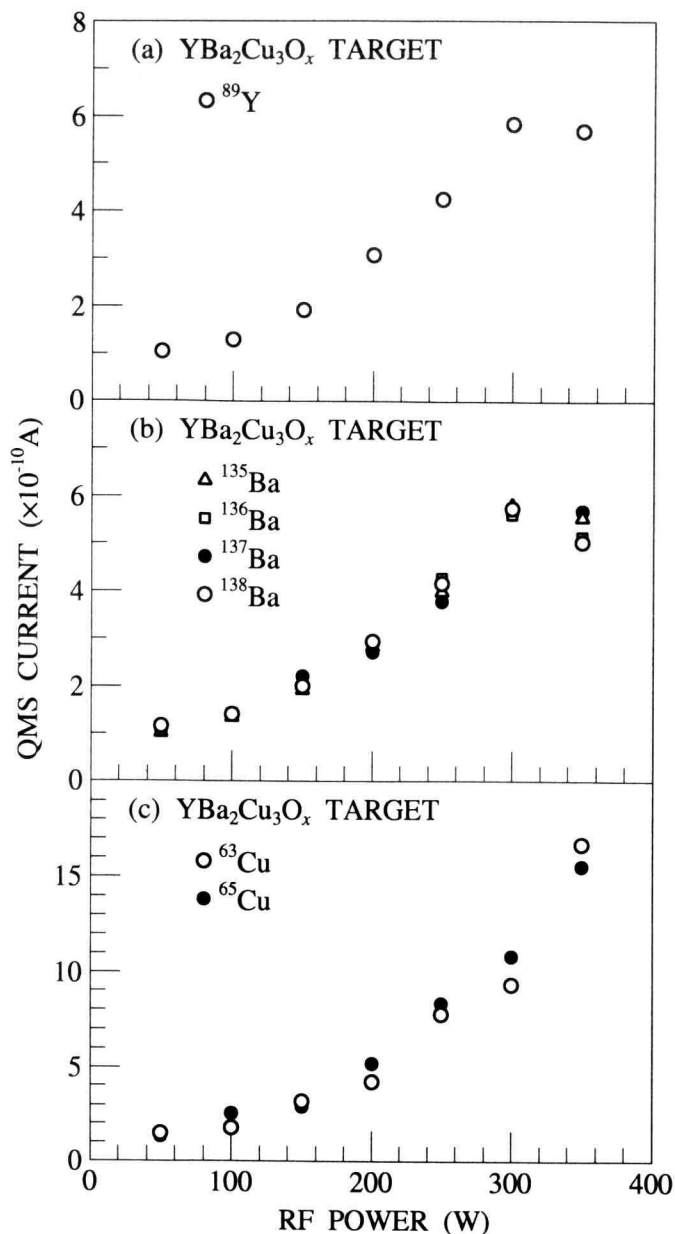


Fig. 6 QMS output current as a function of RF input power for  $\text{YBa}_2\text{Cu}_3\text{O}_x$  sputtered in 80 % Ar / 20 %  $\text{O}_2$  5 Pa atmosphere. (a)  $^{89}\text{Y}$ , (b) Triangles, squares, filled and open circles represent  $^{135}\text{Ba}$ ,  $^{136}\text{Ba}$ ,  $^{137}\text{Ba}$  and  $^{138}\text{Ba}$ , respectively, (c) Open and filled circles represent  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , respectively.

monitor as a function of RF input power in 5 Pa pure Ar atmospheres. The deposition rate is proportional to the RF power of the target. By comparing Fig. 5 with Fig.4, it shows that QMS system can detect sputtered species from the target.

### 3.2 YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> Target

Figure 6 (a) shows the averaged step height of <sup>89</sup>Y as a function of RF input power in 80 % Ar / 20 % O<sub>2</sub> atmosphere for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> oxide target. An isotope of Y is only <sup>89</sup>Y. QMS current of <sup>89</sup>Y increases almost linearly with the RF power of the target.

Figure 6 (b) shows the averaged step height of Ba as a function of RF input power. Isotopes of Ba are <sup>130</sup>Ba, <sup>132</sup>Ba, <sup>134</sup>Ba, <sup>135</sup>Ba, <sup>136</sup>Ba, <sup>137</sup>Ba and <sup>138</sup>Ba. The natural abundance of <sup>130</sup>Ba, <sup>132</sup>Ba, <sup>134</sup>Ba, <sup>135</sup>Ba, <sup>136</sup>Ba, <sup>137</sup>Ba and <sup>138</sup>Ba is 0.1:0.1:2.4:6.6:7.8:11.2:71.7, respectively. In the Figure, only <sup>135</sup>Ba, <sup>136</sup>Ba, <sup>137</sup>Ba and <sup>138</sup>Ba are shown. Triangles, squares, filled and open circles represent to those of <sup>135</sup>Ba, <sup>136</sup>Ba, <sup>137</sup>Ba and <sup>138</sup>Ba, respectively. QMS currents of <sup>135</sup>Ba, <sup>136</sup>Ba, <sup>137</sup>Ba and <sup>138</sup>Ba increase almost linearly with the RF power of the target. The observed values of QMS currents of <sup>135</sup>Ba, <sup>136</sup>Ba, <sup>137</sup>Ba and <sup>138</sup>Ba are almost the same intensities, contrary to the values of the natural abundance of Ba.

Figure 6 (c) shows the averaged step height of Cu as a function of RF input power. Open and filled circles represent to those of <sup>63</sup>Cu and <sup>65</sup>Cu, respectively. QMS currents of <sup>63</sup>Cu and <sup>65</sup>Cu increase almost linearly with the RF power of the target. The observed values of QMS currents of <sup>63</sup>Cu and <sup>65</sup>Cu are almost the same intensities, contrary to the values of the natural abundance of Cu.

Figure 6 shows that these QMS currents of mass number 89, 135, 136, 137, 138, 63 and 65 are not due to Y, Ba and Cu atoms sputtered from YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> target. The detector of this QMS system is a channel-type secondary electron multiplier. If light is incident on a cathode of the secondary electron multiplier, output current increases due to the photoelectric effect<sup>8)</sup>. In this system, however, the plasma emission light may not be incident on the cathode, as this system can detect Cu atoms sputtered from Cu target. The observed QMS currents may be due to species released from the vacuum chamber or diffusion pump oil, decomposed by the RF electric field. The sputter yield of an oxide target is in general rather small<sup>9)</sup>. To detect sputtered atoms, sputter chamber must be evacuated to a higher vacuum.

### Conclusions

In order to clarify the sputtering process, a quadrupole mass spectrometer system evacuated differentially in two stages is developed. To test this system, a copper metal target is sputtered. The system detects <sup>63</sup>Cu and <sup>65</sup>Cu in mass spectra. The observed ratio of <sup>63</sup>Cu to <sup>65</sup>Cu is 7:3, which is close to the value of 69:31 of the natural abundance of copper isotopes of <sup>63</sup>Cu and <sup>65</sup>Cu. This result shows that this system can detect Cu atoms sputtered from Cu metal target. In case of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> target, observed QMS currents of Ba and Cu isotopes are almost the same intensities, contrary to the values of the natural abundance of Ba and Cu. The failure of detecting sputtered species from the

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> target is caused by the small sputtering yield of the oxide target.

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