Predicting the effect of process gas pressure on the elemental composition of magnetron sputtered cuprate films.

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Abstract

A comprehensive study of the effect of process gas pressure on the composition of sputter deposited cuprate superconductors is presented. Magnetron sputter deposition of films from single targets of the cuprate high T_c superconductors $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $La_{1.83}Sr_{0.17}CuO_4$ was used to deduce the effect of deposition conditions on the film composition. Both targets were sputter deposited onto Al foil with the same basic conditions (power, base pressure and deposition time), however, the deposition pressure was altered. Elemental analysis was performed using energy dispersive spectroscopy or wavelength dispersive spectroscopy to determine the ratio of elements in the deposited film. A varying process gas pressure changes the overall deposition rate, and has a major effect on the Bi, Sr and Ca content relative to Cu in films derived from Bi-2212 targets. Bi/Cu linearly increases with pressure - at low pressures the Bi concentration is below ideal values, and increases linearly as the pressure increases to above the ideal. The La-214 composition of the films derived from La214 targets is very pressure independent, but deposits La rich and Sr deficient. A simple model using equilibrium thermodynamics is introduced which is versatile and can be used to help predict the film composition. Collisions with the process gas is the main factor in the observed composition variation between the film and target and the simple throughput model is able to describe this essential aspect, and allow one to

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predict which multielement targets are likely to produce stoichiometric films.

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1. Introduction

A variety of physical vapor deposition techniques are used to deposit cuprate superconducting films, including molecular beam epitaxy (MBE) [1, 2, 3], pulsed laser deposition (PLD) [4, 5] and sputtering [7, 6]. Sputtering is most commonly used because of the smaller start-up and maintenance costs compared with both PLD and MBE. Sputter deposition using multiple oxide targets allow independent control of the deposition rates of various elements. For example, one may use targets composed of BiO, SrCuO, and CaCuO [3] to deposit $Bi_2Sr_2CaCu_2O_{8+\delta}$ thin films. In the majority of cases, however, a single target is used and its stoichiometry is sometimes adjusted to account for differential scattering by the process gas and resputtering of the film by oxygen anions [7, 6].

As a result of the multiplicity of factors influencing the quality of the film, it is difficult *a priori* to predict the success of an experiment. Several factors such as target element binding energies, collisions with process gas molecules, the presence of a multi-element target and the comparatively high kinetic energy of the sputtered particles, make full-blown sputtering simulations an immense undertaking. Instead, an approximate method such as Monte-Carlo simulations is used to generate a representative subset of the system.

The majority of Monte-Carlo simulations study a single element target to predict the expected film deposition rate [8, 9, 10, 11, 12] or structure [10, 11, 13]. Other simulations use multi-element targets and focus on the relationship between the target and film composition [14, 15, 16, 17, 18]. In these simulations, collisions between the target element and the process gas is a major determinant of the film composition. In this letter, we present a simple thermalized gas model to capture the important elements of the problem, allowing one to predict the relationship between the target vs film stoichiometry. Experimental support is drawn from studies of the effect of process gas pressure on DC magnetron sputtered films, using single targets of the superconductors $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) and $La_{1.83}Sr_{0.17}CuO_4$ (La-214). This paper presents the first study of film composition versus pressure for the cuprate superconductors and, in addition, present a model that can be used to predict the potential success of an experiment using multi-element targets.

2. Experimental

To synthesize Bi-2212 targets Bi_2O_3 (99.975%, Alfa-Aesar), $SrCO_3$ (99.99%, Alfa-Aesar), CaO (99.95%, Alfa-Aesar) and CuO (99.7%, Alfa -Aesar) were mixed in the appropriate stoichiometric ratios and ground for two hours using an agate auto grinder. The mixture was placed in an Al_2O_3 crucible and reacted in air inside a Thermolyne 48000 box furnace. The first reaction, which calcinate the powders, is at 800 °C for 12 h (slow heat/slow cool at 4 °C/min). After the first reaction, the powder is ground for two hours. The next two reactions are also in air at a temperature of 870 °C. In between the latter two reactions the powder is ground for two hours, and finally sifted through a 70 μm sieve. Approximately 40 g of the sieved powder was pressed into 5 cm diameter by 0.5 cm thick disc using a pressure of 8500 psi, then sintered for 30 hrs at 875 °C to harden the target and reduce porosity. The La-214 target is synthesized in a similar manner, except calcination was completed at 800 °C while reaction and sintering is completed at 1000 °C. Precaution was taken to dry La_2O_3 (99.99%, Alfa-Aesar) in air @ 1000 °C for 12 hours prior to use.

A Corona Vacuum Coaters V-3T sputtering system, equipped with five magnetrons configured in a side-sputtering arrangement (on-axis), was used. A rotatable substrate table is located directly across (5.5 cm) from the targets. To power the magnetron an Advanced Energy MDX-1 K DC supply is used for both the Bi-2212 and the La-214 targets. The film was deposited onto water cooled substrates to which is affixed aluminum foil strips on glass microscope slides. Ten substrates were arranged on the table (43 cm diameter), equally spaced by 30° degree. A -20 V bias was applied to each piece of Al foil using a carbon brush assembly detailed here [19]. The Bi-2212 and La214 targets were sputtered using a DC power of 60 W or 55 W, respectively. Prior to sputtering a base pressure of $(5\pm1)\text{x}10^{-7}$ Torr is achieved. Both targets were sputtered under various process gas pressures to determine the effect of the sputtering conditions on the composition of the resulting films. A physical mask is placed over the target to limit the deposition to a single substrate, and subsequent depositions are made by simply rotating the table 30°.

Composition of the films was determined using energy dispersive spectroscopy (EDS) measurements employing a JEOL JXA-8200 Superprobe equipped with a Noran energy detector (0.133 keV energy resolution). A 7 keV electron beam was used to measure the EDS spectra of Bi-2212 films while a 5 keV beam was used to measure the La-214 films. The Al foil strips were removed from the microscope slides and placed on an Al base using double sided Cu tape. A 10 μm spot of the film was measured for each point and the compositions are determined following ZAF correction.

3. Results and Discussion

3.1. Experiment

The first target used was Bi-2212. Multiple depositions were made using the sputtering conditions listed in Table 1.

Table 1: Deposition Conditions for the Bi-2212 and La-214 targets

	Bi-2212		La-214	
sample #	P (mTorr)	Ar:O_2	P (mTorr)	Ar:O_2
1	27.1	20:20	30	30:15
2	22.8	14:28	25	24:12
3	19.9	15:15	20	22:11
4	17.1	10:20	16	15:7
5	14.4	10:10	13	12:6
6	13.3	10:05	10	9:4
7	14.2	8:16	8	5:2
8	11.3	6:12	6	3:1
9	8.5	5:5	4	3:1
10	7.25	3:9	2	3:1
11	0.9	1:0	0.8	2:1

Figure 1 shows a set of EDS data for the Bi-2212 target, while Figure 2 shows the La-214 EDS data.The scatter present in the data is typical for all the data sets run. At lower pressures the scatter is reduced due to the increased film thickness. It is clear to see that the Bi2212 film (Figure 1) is deficient in Sr and Ca (Bi/Cu$\approx$1.05, Sr/Cu$\approx$0.75 and Ca/Cu$\approx$0.3 should be 1, 1 and 0.5 respectively); whereas the film deposited from the La-214 target is rich in La (La/Cu $\approx$2.2), and deficient in Sr (Sr/Cu$\approx$0.09).

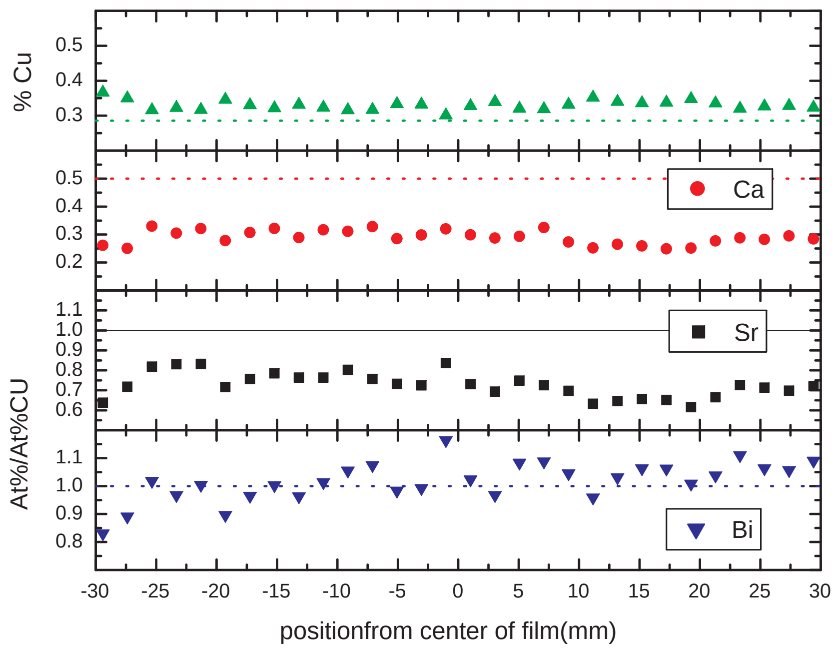

Figure 1: EDS of sample 3 from the Bi-2212 target run (See Table 1 for deposition conditions). The solid lines represent the expected composition from the target stoichometry.

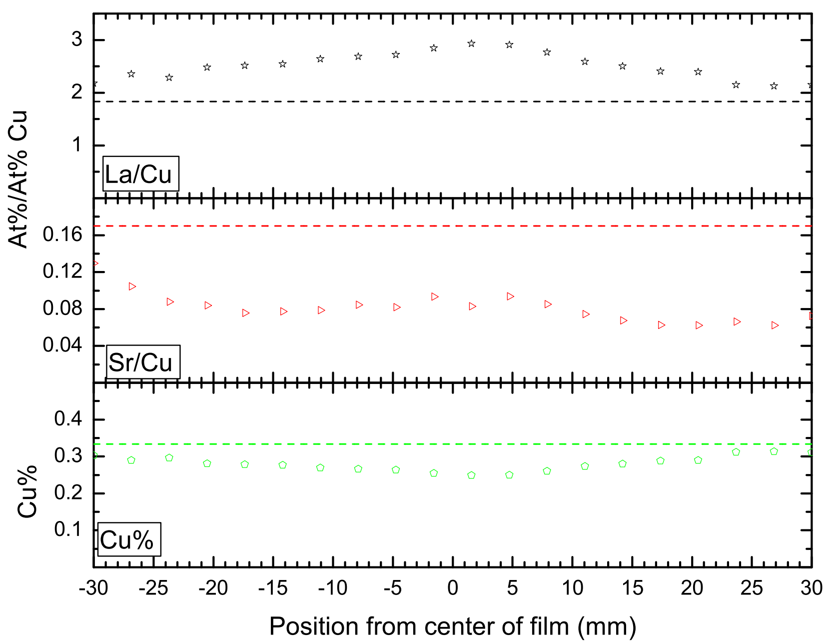

Figure 2: WDS of sample 1 from the La-214 target run (See Table 1 for deposition conditions). The solid lines represent the expected composition from the target stoichometry.

Besides looking at ratios of Bi, Sr and Ca with Cu a fourth statistical quantity was calculated, the ratio of Cu to all the other elements in the film,

$$Cu\% = \frac{At\%Cu}{At\%Cu + At\%Bi + At\%Sr + At\%Ca} \tag{1}$$

A statistical analysis of the composition data was performed for all depositions. The values were first normalized to Cu, the mean value of the elemental concentrations across the film calculated, as well as the maximum and minimum values. In Figure 2 the effect of oxygen resputtering on the La-214 film is seen in the Cu% panel. As discussed elsewhere [19], the on-axis sputtering geometry often leads to resputtering of the deposited film by energetic anions. This effect is also seen in the Bi-2212 films as the pressure decreases. In cases where the film composition is drastically altered by resputtering, the effected data was removed from the statistical analysis. In such cases the first and last 5 data points were used to calculate the film compositions.

Figure 3 presents the elemental means for Bi/Cu, Sr/Cu, Ca/Cu and Cu% under the sputtering conditions shown in Table 1. The main trend that is displayed in Figure 3 is the linear increase of Bi/Cu concentration as the chamber pressure increases. This phenomenon is believed to occur because the heavier Bi particles, with their larger energy, can sustain more collisions with the lighter gas molecules between the target and the substrate and still reach the substrate. The medium elements (Sr and Cu) are comparable and therefore consistently deposited as the process gas pressure increases, while Ca is seen to have a slight up turn at lower pressures.

Figure 4 presents the La/Cu, Sr/Cu and Cu% values for La-214 runs listed in Table 1. The obvious trends shown in Figure 4 are that all the films are La rich, and Sr deficient, but the Cu% values are close to the desired value. Unlike the Bi-2212 films the concentrations of La and Sr are relatively stable as the deposition pressure varies. It is clear that even though La-214 and Bi-2212 are both cuprate superconductors their sputtering properties are very different.

3.2. Model

To explain the trends found in the experimental data a simple model was developed. The model adjusts the equilibrium mean free path of a thermalized gas particle [20], to represent the mean free path of a target particle in a dense gas. In this model the radius of interaction of a gas-gas collision is

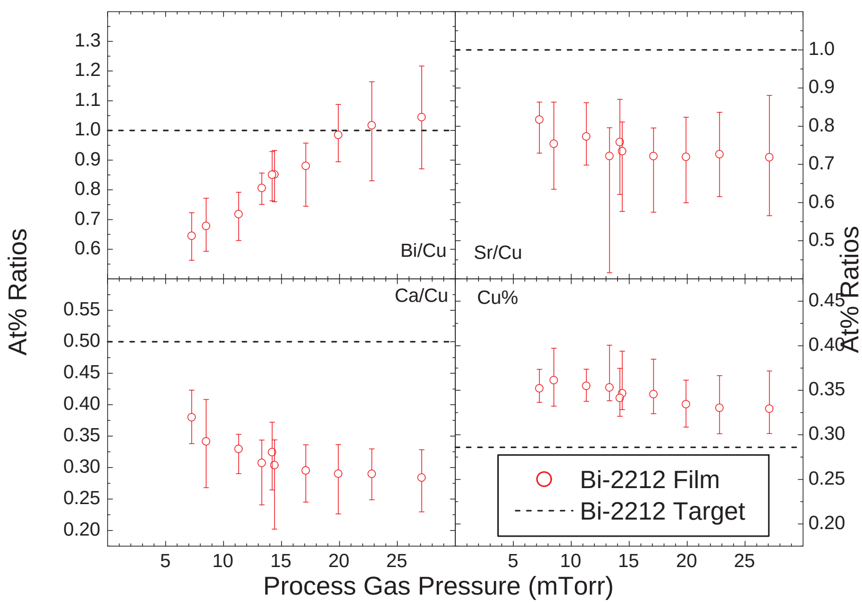

Figure 3: Elemental concentrations of Bi, Sr and Ca normalized to Cu versus deposition pressure. Also shown is the calculated Cu% values. The solid lines represent the expected composition from the target stoichiometry.

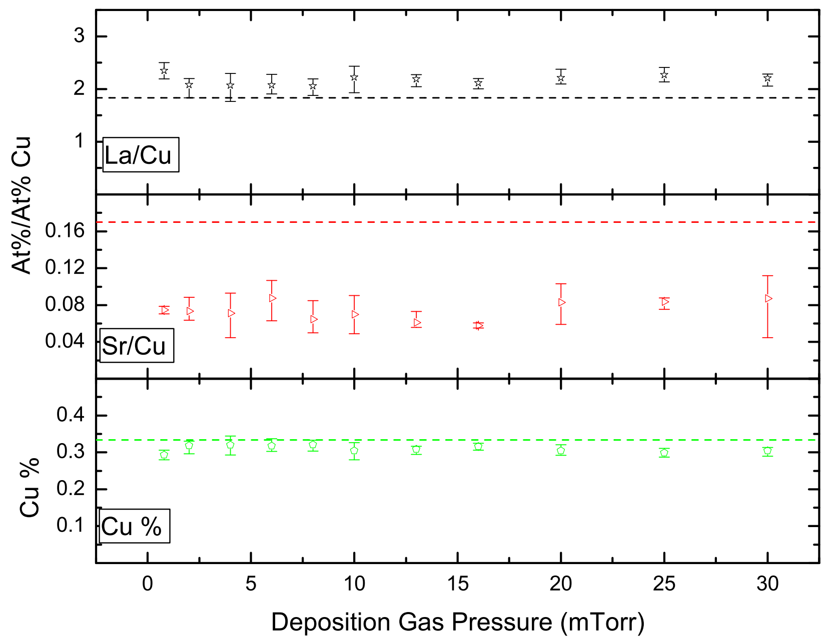

Figure 4: Elemental concentrations of La and Sr normalized to Cu and the Cu% values versus deposition pressure. The solid lines represent the expected composition from the target stoichiometry.

replaced with the collision radius of a gas-particle pair. The mean free path of a target particle would then be described by Equation (2):

$$\ell = \frac{1}{\sqrt{2}\pi n(r_e + r_g)^2} \tag{2}$$

where ℓ is the mean free path, n is the process gas number density and r_e and r_g are the atomic radii of the target element and the process gas. This expression is similar to that used by [17, 12] for their Monte-Carlo simulations. Atomic radii (calculated values) were obtained from www.webelements.com [21]. Using an Ar gas temperature of 300 K and the Ideal Gas law the gas number densities (n) were calculated (=P/kT).

To account for collisions of the particle with the gas we defined a parameter named Throughput,

$$T = \frac{\ell M_e}{M_g} \tag{3}$$

The Throughput (Equation (3)) is a measure of the proportion of a target element that will make it through the process gas to the substrate, where M_e and M_g are the mass of a target element and process gas particle respectively.

Table 2: Constants for Throughput calculations. Atomic radii are from webelements and use calculated values (empirical values in brackets). In the case of La the empirical value is used.

Element	Atomic Radius (pm)	Mass ($\times 10^{-25}$ kg)
Ar	71.0 (-)	0.66
Bi	143 (160)	3.47
Sr	219 (200)	1.45
Ca	194 (180)	0.67
La	- (195)	2.31
Cu	145 (135)	1.06

Figure 5 shows the calculated values of T for Bi, Ca, Sr, La and Cu in Ar. The figure shows that Bi, with the highest T, will be deposited more than Cu, Sr or Ca, which was is indeed what is observed in the experimental data. Also Ca, with the lowest T value, is the most deficient element in the deposited film. The T values for Sr, La and Cu are close and this could

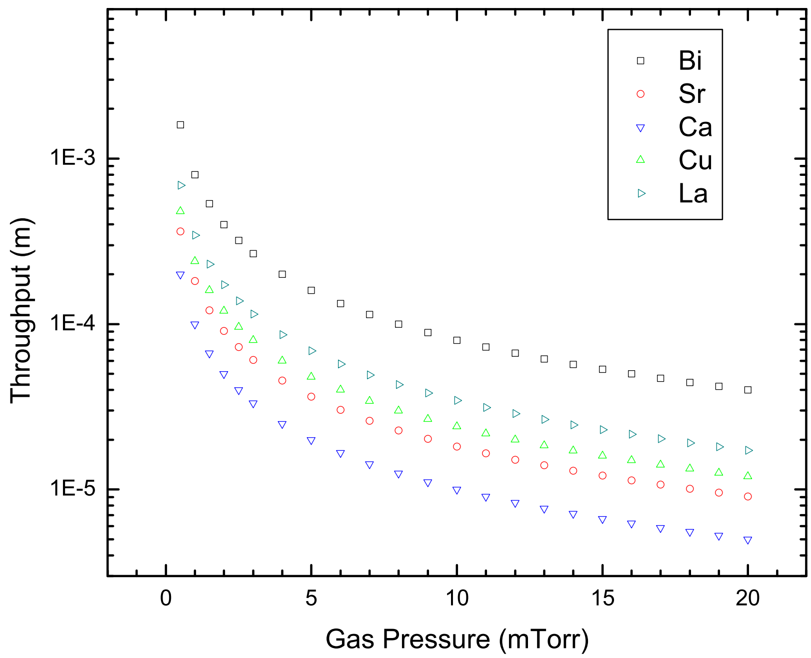

Figure 5: Throughput of Bi, Sr, Ca and Cu in an Ar gas

explain why Sr is only slightly deficient in Bi-2212 films, and the composition remains fairly consistent for the La-214 target.

The ratio of Throughputs for each element relative to another (say Cu) is independent of pressure because, according to equation 2 and 3 it is simply a ratio of element masses and radii. The experimental data for La214 is entirely consistent with this prediction, whereas this is only true for Sr and Ca when sputtering Bi2212. On the other hand Bi shows a behavior inconsistent with the model. It could either be that the absolute Bi content is constant while the Cu content decreases linearly with pressure in a manner similar to Ca and Sr; or that the Bi content is increasing linearly with pressure. The latter suggestion is unphysical in the dense gas regime. However, the La214 composition ratios are constant for all elements relative to Cu and this would require that all elements experience a decrease in throughput with increasing pressure. Thus it seems likely that the rate of decrease of the Bi throughput with pressure is smaller than that of all other elements. Evidence for this comes from sputter deposition of Bi and Cu, where it is seen that Bi enters the dense gas regime (where its deposition rate decreases with pressure) at at a higher pressure than Cu. From table 2 it is clear that bismuth has the smallest radii and largest mass, making it the least likely to interact with the process gas and more likely to sustain it's momentum in a collision with the lighter process gas particle. Altogether it is evident that the simple throughput model represents the trends observed in the data, and the sole deviation from the expected trend can be explained. The throughput model also predicts $YBa_2Cu_3O_{7-\delta}$ to be favourable for multielement target sputtering and this is borne out in experiment.

4. Conclusions

Using a simple thermalized gas model, we have obtained a good understanding of the effect of the process gas on the composition of films deposited from multi-element targets of the cuprate superconductors. The proposed model explains the trends found in the experimental data in the dense gas regime. This simple approach allows one to determine what multi-element targets can be used for sputter depositions. Consistent with the model attempts to deposit Bi2212 films result in deficiencies of Ca and Sr. For the La-214 target, varying the deposition pressure did not have any significant effect on the composition of the deposited film, however the film is rich in La and deficient in Sr, consistent with the model. Sputter deposition of Bi2212 is consistent with the model if one takes account of the unique combination of radii and size of Bi. Collisions with the process gas is the main factor in the observed composition variation between the film and target and the simple throughput model is able to describe this essential aspect, and allow one to predict which multielement targets are likely to produce stoichiometric films.

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