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# Raman scattering spectroscopy as a characterization method of coated conductors

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*Abstract*-- **The purpose of this work is to develop, integrate, and implement an optical characterization method to evaluate physical properties in coated conductors and investigate the local distribution of the causes of degraded performance. The method that we selected at this moment is Raman scattering spectroscopy, which is accompanied with measurements of local supercurrent transport, phase composition, microstructure, and epitaxy quality for coated conductors that range in size up to multi-meter-length tapes and that embrace the entire tape embodiment (substrate through cap layer). The establishment of Raman spectroscopy as an on-line process monitoring tool is our eventual goal of research, but it requires very robust and cost-effective equipments. We analyzed $YBa_2Cu_3O_7$(YBCO) thin films grown at various substrate temperatures by using Raman spectroscopy. YBCO films were grown by a high-rate electron-beam co-evaporation method. Raman spectra of YBCO films with lower-transport properties exhibit additional phonon modes at ~300 $cm^{-1}$, ~600 $cm^{-1}$, and ~630 $cm^{-1}$, which are related to second-phases such as $Ba_2Cu_3O_{5.9}$ and $BaCuO_2$. We propose a new method to characterize Raman spectra of coated conductors for an in-line quality control.**

## 1. INTRODUCTION

There have been strong research activities regarding YBCO coated conductors due to their possible applications to magnets, motors, fault-current limiters, transformers, transmission lines, and so on [1-3]. For large-scale commercialization, however, more economical and effective growing method is required. High-rate *in-situ* YBCO film growth was demonstrated by means of the electron beam co-evaporation [4]. Even though our oxygen pressure is low (~ 5 x $10^{-5}$ Torr), we can synthesize as-grown superconducting YBCO films at a deposition rate of ~10 nm/s. Relatively high temperatures of around 900 °C was necessary in this process so far, and it suggests that this temperature at a given oxygen activity allows Ba-Cu-O liquid formation along with an YBCO epitaxy. Local critical current density shows a clear correlation with local resistivity [5]. Raman scattering spectroscopy has been known to be a valuable tool for structural and chemical characterization of high-$T_c$ superconductors [6-7]. Recently, Gonzalez *et al.*, used micro-Raman scattering spectroscopy to evaluate local uniformity of the uniaxial texture of YBCO coated conductors and successfully determined the degree of biaxial texture quantitatively [8]. In this study, we propose micro-Raman scattering as an effective tool to monitor YBCO coated conductors in terms of chemical homogeneity in micrometer scale, which provides crucial information regarding obtaining the optimal growth conditions for good-quality YBCO films.

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## 2. EXPERIMENTS

YBCO films have been grown by high-rate electron-beam co-evaporation method. Films were grown by means of electron beam co-evaporation of Y, Ba and Cu metal sources in oxygen atmosphere, or so-called reactive co-evaporation. Y and Ba metal evaporation rates were controlled by laser atomic absorption sensors, and the evaporation of Cu by chopped ion gauge monitor. Molecular oxygen was introduced in two ways: into the growth chamber background in general and alternatively by means of 1" diameter nozzle directed to the substrate surface to enhance the flux. A 500 W halogen-lamp-based radiation heater could heat the sample holder to 1000 °C. Most films were grown in a system background pressure of 5 x $10^{-5}$ Torr regardless of the nozzle or general chamber use, at oxygen flow rate of around 35 sccm for the general case, and 52 sccm for the nozzle case. Temperatures ranging from 860 to 1000 °C were explored in this report; a much wider range was used in developing the process. By turning off the heater and introducing a high flow rate of oxygen immediately after the deposition, the samples were cooled down quickly (to 300 °C in 2 minutes), as the pressure reached up to 100 Torr. *In-situ* oxygen loading was performed at 300 °C in 300 Torr for 30 min under ozone-containing oxygen (approx. 8 % at the generator) to improve $J_c$ by over-doping. The thickness of the films is about 500 nm. It is shown by x-ray diffraction (XRD) that the as-grown YBCO films have a highly c-axis oriented and in-plane aligned texture.

Room temperature Raman-scattering measurements were performed using a JY TRIAX 550 spectrometer equipped with a nitrogen-cooled CCD array detector as shown in Fig. 1. The samples were excited with 50 mW of the 514.5nm line of an Ar-ion laser, focused to a 100 μm diameter spot. For micro-Raman scattering measurements, a microscope objective lens (x 60) was used to focus the

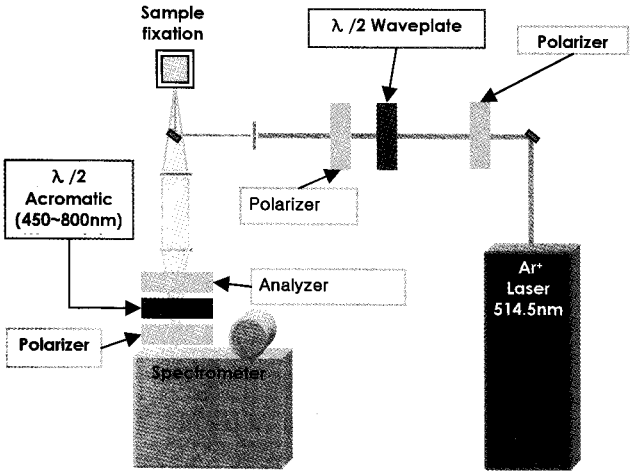


Fig. 1. Measurement set-up for Raman scattering spectroscopy.

laser. In this case, the focused spot was estimated to be 1~2 microns at best.

When necessary, the spectra were obtained with the incident and scattered light polarized in the following configurations in order to identify the symmetries of the excitations studied: $(\mathbf{E}_i,\mathbf{E}_s) = (\mathbf{x},\mathbf{x})$: $A_g$; $(\mathbf{E}_i,\mathbf{E}_s) = (\mathbf{x},\mathbf{y})$: $B_{1g}$; $(\mathbf{E}_i,\mathbf{E}_s) = (\mathbf{x}+\mathbf{y},\mathbf{x}+\mathbf{y})$: $A_g+B_{1g}$; $(\mathbf{E}_i,\mathbf{E}_s) = (\mathbf{x}+\mathbf{y},\mathbf{x}-\mathbf{y})$: $A_g+B_{1g}$; where $\mathbf{E}_i$ and $\mathbf{E}_s$ are the incident and scattered electric-field polarizations, respectively, **x** and **y** are the [100] and [010] crystal directions, respectively, and where $A_g$,and $B_{1g}$ are the singly degenerate irreducible representations of the YBCO space group ($D_{2h}$ -*mmm*).

## 3. RESULTS AND DISCUSSION

Fig. 2 illustrates the x-ray diffraction (XRD) measurements of the YBCO samples. In order to correlate the variation of the oxygen contents with the crystal structure, and to get further confirmation on the oxygen contents, we analyzed the XRD patterns of our samples and compared these with the dataset in the YBCO XRD database. The XRD 2θ patterns are shown in figure for these five kinds of YBCO films. XRD results cannot distinguish the quality of the samples. From this, we can conclude that all the samples have the same crystal orientation of YBCO structure.

Raman scattering spectra of YBCO films are shown in Fig. 3. All five spectra include the well-known YBCO phonon modes at ~340cm$^{-1}$ (YBCO $B_{1g}$) and ~500cm$^{-1}$ (apical oxygen). These modes are associated with the out-of-phase vibration of the O(2)-O(3) oxygen atoms in the $CuO_2$ planes (~340cm$^{-1}$) and the vibration of the apical oxygen O(4) atom (~500cm$^{-1}$), respectively [9-10]. The frequency of the apical oxygen (AO) mode is known to provide an approximate measure for the oxygen stoichiometry of the YBCO films [11]. It is well-known that for tetragonal YBCO, the AO frequency is near 480 cm$^{-1}$, whereas for the orthorhombic form, which is

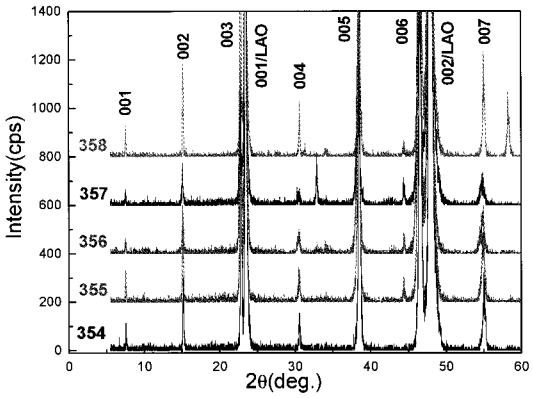


Fig. 2. X-ray diffraction (XRD) data from 5 different YBCO films.

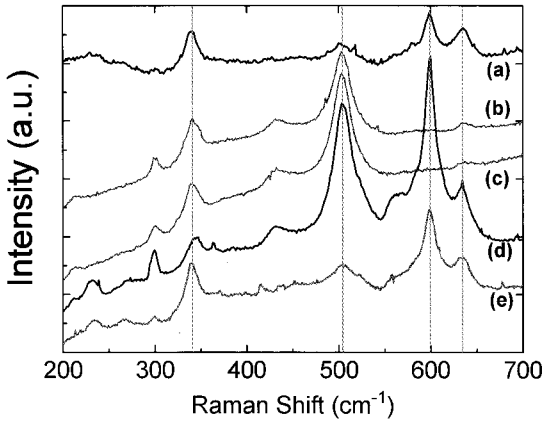


Fig. 3. Raman scattering spectra taken from 5 different YBCO films: (a) from #354, (b) from #355, (c) from #356, (d) from #357, and (e) from #358, respectively. The spectra are offset for clarity.

expected to be fully oxidized, the AO frequency is near 500 cm$^{-1}$. Thus, the samples we studied are all seemed to be orthorhombic.

There are, however, additional phonon features present, among which three modes are most apparent: One is near 300 cm$^{-1}$, which is related to CuO [12], another is near 600 cm$^{-1}$, which is related to $Ba_2Cu_3O_{5.9}$ [6], and the third is near 630 cm$^{-1}$, which is related to $BaCuO_2$ [7]. This result shows that Raman scattering is very sensitive in detecting second-phases in the films of interest. In fact, we can classify the spectra into two groups according to the observed phonon modes: Group I include (a) (sample #354), (d) (sample #357), and (e) (sample #358), which show the second-phase (Ba-Cu-O) related modes as well as the YBCO modes. Group II include (b) (sample #355) and (c) (sample #356), where only the YBCO modes are observed. Since the data taken from different samples in each group are very similar, we only show data from one sample from each group, #354 from Group I and #356 from Group II, hereafter, for simplicity and clarity.

Fig. 4 shows the surface morphology of sample #354 and #356 films taken from a scanning electron microscope (SEM). We can immediately observe that each sample "looks" different. From the pictures, sample #356 seems to be more homogeneous, or "smoother" than sample #354. Note that, however, no significant difference between #354 and #356 was observed from the XRD data shown in Fig. 2, which indicates that basically they have the same global crystal structure and that in the length scale which XRD measures those two samples are rather similar, if not the same. Whereas, SEM micrographs (Fig. 4) clearly show that the homogeneities of the two samples might be different, and Raman spectra (Fig. 3) imply that the two samples (spectra (a) and (c)) are indeed quite different chemically as well: For example, #354 exhibits second-phase (Ba-Cu-O) related mode but #356 does not.

In Fig. 4(b), the big grain is composed of Ba-and Cu-rich compounds (Y:Ba:Cu = 0: 1:4.29) while the other region is found to be Y-rich but Ba-and Cu-poor composition (Y:Ba:Cu = 1:1.30:2.54) as measured by energy dispersive x-ray analysis. This observation is consistent with our intention to control the materials with Ba-poor composition during the deposition [4]. One of the reasons why the different techniques "observe" different aspects from the same sample depends on the "range" of the measurements. SEM micrographs and the Raman scattering are "local" tools for measuring material properties, whereas XRD measures global properties.

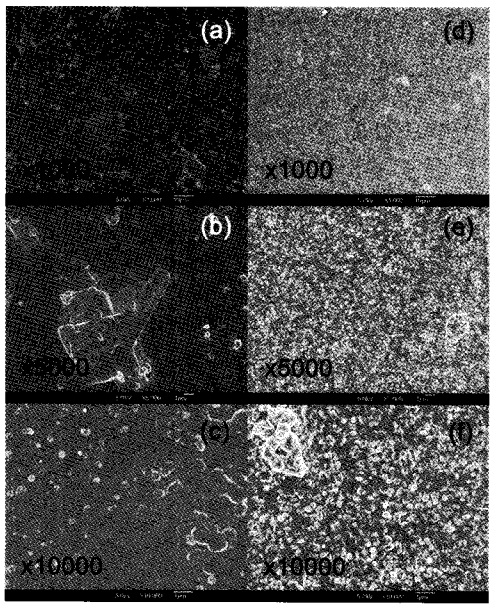


Fig. 4. SEM micrographs of #354 ((a), (b), (c)) and #356 ((d), (e), (f)) in the different magnifications. The magnification for (a) and (d) is x1,000, that for (b) and (e) is x5,000, and that for (c) and (f) is x10,000, respectively.

In other words, it seems that the YBCO films we measured look essentially the same in the large length scale but they do look different and behave differently in small length scales (less than 100 μm, for our case). If this statement is correct, then we seem to have a very powerful local measurement too l, Raman scattering, to characterize the local variations, especially chemical ones, in the seemingly homogeneous YBCO films. In order to confirm this idea, we performed micro-Raman scattering measurements on the 354 and 356 YBCO films, in which a few micrometer scale characterization are possible.

One of the novelties of the approach used in adaptation of Raman spectroscopy to on-line monitoring of YBCO deposition is that the Raman spectra are collected on moving tape in a notch filter, using the charge-coupled device (CCD) detector as the monochromator. Therefore, as the tape moves under the optical element that concurrently focuses the laser on the tape surface and collects the Raman scattered radiation from the YBCO film, an average Raman spectrum is collected for a fixed length of tape without bothering speed of the production. For the measurements on moving tapes reported in this paper, the tape travel speed can be faster than 100 m/h. The focal length of the collection optic at the tip of the probe is 11 mm and no attempt has yet been made to maintain a specific focus level on moving tape segments. Nonetheless, the spectral quality and reproducibility achieved thus far have been of sufficiently high quality to provide useful information. The vast majority of spectra exhibit the same peak and baseline count levels and the same overall spectral features, but on occasion random aberrant spectra are recorded.

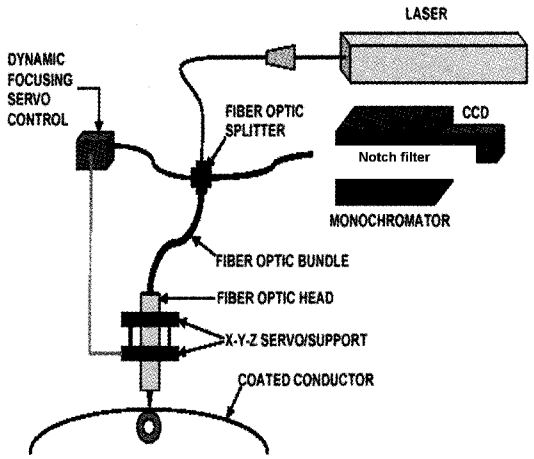


Fig. 5. Reel-to-reel in-line characterization set-up of coated conductors using Raman scattering with a notch filter.

## 4. CONCLUSION

We have measured Raman scattering responses from YBCO films grown by high rate e-beam co-evaporation. The measurements show that the samples are c-axis oriented. Some of the samples show second-phase-related phonon modes at 300 $cm^{-1}$, 600 $cm^{-1}$, and 630 $cm^{-1}$, which are related to second phases such as Cu-O and Ba-Cu-O, in addition to the YBCO modes at 340 $cm^{-1}$ and 500 $cm^{-1}$. The frequency of the AO phonon mode, which is a sensitive measure of oxygen content, was measured to be 500 $cm^{-1}$, which suggests that these films are orthorhombic. From these results, we can use Raman scattering as a good detector for second-phases and oxygen contents in the YBCO films. Moreover, using a notch filter, we could easily monitor the quality of newly produced coated conductor tapes.

## ACKNOWLEDGMENT

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