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Depth Raman spectra and laser-induced structural and oxygenation changes in thick $YBa_2Cu_3O_{7-\delta}$ films

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We describe an experiment of inducing structural and oxygenation changes in small volumes of a thick $YBa_2Cu_3O_{7-\delta}$ (YBCO) film by subjecting the film to a focused Ar laser beam used as the pump source for a depth profiling Raman scattering system. The laser-induced changes were evidenced by high spectral and spatial resolution Raman spectra taken at different depths of the film, before and after the films' exposure. The irradiation and the measurement were done at room temperature in a regular air environment.

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1. Introduction

Soon after YBCO discovery, the Raman technique has imposed itself not only as a powerful tool for non-destructive identification of the structural and of other characteristics leading to superconducting properties (as, for example, the oxygen content), but also as a valuable technique to induce oxygen diffusion and phase changes in YBCO films utilizing the laser of the Raman system [1].

Modern Raman measurement systems combine high spectral resolution with high spatial (lateral and in-depth) resolution by using the confocal configuration at detection. Apparently using this technique to study properties of YBCO films looks difficult because the penetration depth of the visible light in YBCO is ~ 100 nm (calculated after ellipsometric measurements reported in [2]). This is a value much smaller than the in-depth resolution of the confocal configuration of such a Raman system, of the order of 1 μm - 1.5 μm. However, previous reports show a high Raman signal response of YBCO films when excited with the 488 nm light of an Ar laser, at least for the most important Raman shift, with the peak near 500 cm^{-1} [3]. This can partially explain the relatively high Raman signals reported in this paper for our thick (1700 nm) YBCO film and the possibility to discern between the 50 spectra taken in the depth of the film. For the small laser spot available from a micro-Raman system, also of micrometer-scale size, the YBCO films appear to be single crystal-like, evidencing the epitaxial micro-scale crystalline structure and the homogeneity of the film, and perhaps contributing also to the good Raman signal that was observed.

In two previous papers we have reported the *in-situ* growth of YBCO films, both *c*-axis and *a*-axis oriented, on $LaAlO_3$ (LAO) substrates, by pulsed laser deposition (PLD), using a kinetic cool-down regime technically more advantageous than the usual one. Good superconducting properties and critical temperature in the limits of 87 K – 90.4 K were obtained without a high temperature post-deposition annealing process [4-6].

In this paper we report results after performing depth profiling Raman spectra on an YBCO thick film, obtained *in-situ* as above mentioned, with the thickness of about 1.7 μm and with a critical temperature of ≈ 88 K. We measured Raman spectra at up to 50 different depths in this film before and after locally irradiating the film by the Ar-laser beam used as a pump source of the Raman system, on the very same spot on the film. We used the 488 nm excitation wavelength and YBCO's Raman resonance properties at this wavelength. Thermally-induced effects inside the film manifested as changes in the oxygen content show nicely on the Raman spectra. These spectra were taken at different depths inside the film, on small areas of the order of several μm^2 and at depths smaller than the pump laser depth of focus (~ 1000 nm) and smaller than the depth of detection capability (also ~1000 nm). The results encourage us to hope that this technique, besides its diagnostics capabilities, might become a possible new approach to configure superconducting junctions and other electronic devices based on YBCO films.

2. Experiments

We irradiated for 25 minutes, at room temperature, in the environment atmosphere (air), a sample of a thick YBCO film (thickness approximately 1700 nm) grown by PLD on a LAO substrate [5], with a tightly focused 2 mW radiation at 488 nm from a single-mode Ar-laser, to prevent any damage of the sample. The laser is the pump laser used in a Horiba Jobin Yvon Raman system type LabRAM HR800. The Olympus 100x objective that is used has a numerical aperture of 0.9. We performed the Raman spectra before (41 spectra) and after (50 spectra) the laser irradiation of the sample, at different depths inside the films' thickness. The measurements (before and after irradiation) and the irradiation were done on the same location on the YBCO film sample. The LabRAM HR800 system has about 1.5 cm^{-1} spectral resolution and a confocal microscope configuration for detecting the Raman signal, performing as a depth profiling system. The depth of focus of the microscope objective for the pump laser beam is approximately 1 µm. The confocal arrangement at detection provides a precise control of the lateral and of the in-depth position on the film to be measured. The detection system has a lateral spatial resolution of ≥ 0.5 µm and an in-depth spatial resolution of the order of 1µm. The vertical movement of the microscope objective, piezoelectrically controlled has a mechanical resolution better than 10 nm.

3. Results and discussion

YBCO films are highly anisotropic and are sensitive to the polarization geometry of the Raman system. When the laser beam is propagated along the *c*-axis direction, the modes' vibrations manifested as Raman shift peaks at approximately 149 cm^{-1}, 221 cm^{-1}, 337 cm^{-1}, 500 cm^{-1}, and 580 cm^{-1} are permitted [7]. The most significant mode is attributed to the vibrations of the O$_{\text{apex}}$ in the *c*-axis direction, corresponding to the Raman shift peak around 500 cm^{-1}. The position of this Raman shift peak, determined by the δ oxygen coefficient and the corresponding crystalline structure of the YBCO films is strongly correlated with their superconducting properties, e.g., with the value of their critical temperature [8]. We use here two well-known features of the Raman spectra of YBCO to monitor the oxygen coefficient δ and also the oxygen order in O (1) and (5) sites of an YBCO film: the Raman shifts at 580 cm^{-1} and 500 cm^{-1}, respectively. Ref. [1] identifies that the oxygen disorder (through diffusion) gives rise of the 580 cm^{-1} peak intensity that is permitted only in the tetragonal, non-superconducting state.

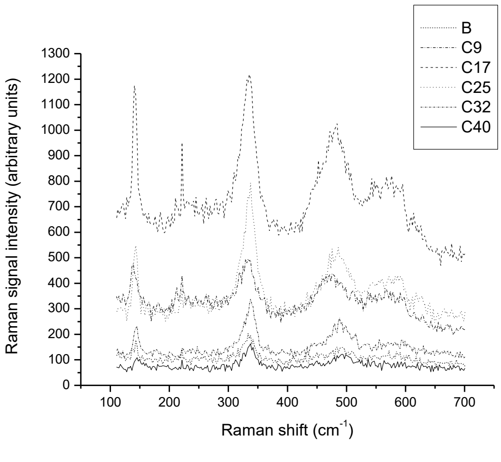

Fig. 1. Raman spectra at 6 different depths of a thick YBCO film before the 488 nm Ar laser irradiation.

Fig. 1 illustrates 6 (chosen from 41) Raman spectra performed at different depths in the YBCO film sample before irradiating the film with the Ar-laser of the Raman system. The 6 (chosen from 50) spectra in Fig. 2 were performed on the same film, in the same point, but after 25 minutes of Ar-laser irradiation. In Fig. 1 the spectra were recorded by moving the microscope objective from the film surface toward the film's substrate (from upper to lower levels of the film, scans noted B, C1 - C40, respectively), while in Fig. 2 the movement was from the lower level of the film upward (scans noted B, C1 - C49, respectively).

The spectra corresponding to the film layers approaching the LAO substrate are gradually weaker as the pump laser light is gradually absorbed in the thick YBCO film. The emitted Raman light of these deep layers of the film is much weaker, first because of the weaker pumping light exciting them, and second because it needs to cross upward the whole thickness of the YBCO film toward the detecting system, and is itself attenuated by the absorption in the YBCO film. On the other hand, the spectra corresponding to layers close to the film's surface are also weaker because the Raman signal is collected from a smaller number of layers. In both, Fig. 1 and Fig. 2, the highest Raman signal corresponds to layers somewhere in the middle of the YBCO film (for Fig. 1 it corresponds to the scan #18 (or C17) out of 41 scans, counted from film's surface downward, and for Fig. 2 it corresponds to the scan #32 (or C31) out of 50 scans counted from the lowest level where the objective stopped after the previous scan, toward the film's surface.

Fig.1 shows scans performed on the film before irradiation. We can observe that the peaks at 143 cm^{-1}, 221 cm^{-1}, 337 cm^{-1}, and 575 cm^{-1} have approximately the same Raman shifts and the same intensity relative to each other for each scan. As we look at the scans from the middle of the film, where the Raman signal is maximum (scan C17), to its surface (scan B), the peak nearby 500 cm^{-1} shifts from 495 cm^{-1} to 487 cm^{-1}, probably due to the oxygen loss near the surface. Note that the depth profiling Raman spectra were recorded about 8 months after the film was grown and some oxygen loss at the film's surface is reasonable to expect.

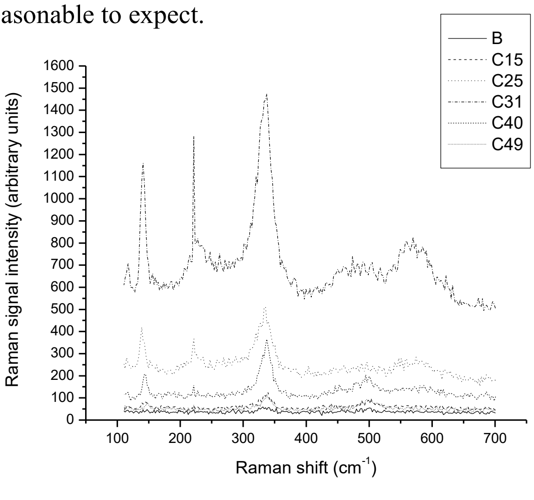

Fig. 2. Raman spectra at 6 different depths of a thick YBCO film after the 488 nm Ar laser irradiation.

Fig. 2 shows scans performed on the film after 25 minutes of the Ar-laser irradiation. One can observe that the peaks at 143 cm^{-1} and 337 cm^{-1} have almost the same Raman shifts and relative intensities to each other. The peak nearby 500 cm^{-1} is broader and shifted from 498 cm^{-1} to 477 cm^{-1} looking from the substrate toward film's surface, due to the heating laser effect contributing to loss of oxygen. There is also an increase in the relative intensity of the 221 cm^{-1} and 570 cm^{-1} peaks as compared to the intensity of the 500 cm^{-1} peak looking from the layers near substrate toward film' surface, accompanying the above mentioned shift of the 500 cm^{-1} peak. These two complementary effects confirm the oxygen diffusion identified in Refs. [1,7] as a result of the laser heating effect.

Fig. 3 compares the highest Raman signal spectra: the spectrum #17 from Fig. 1 (black curve) and the spectrum #31 from Fig. 2 (red curve). We observe that the two spectra differed only as spectral fingerprint not in their intensity. We find again, but more accentuated, the two complementary effects that confirm the oxygen diffusion identified in Refs. [1,7] due to the laser heating effect.

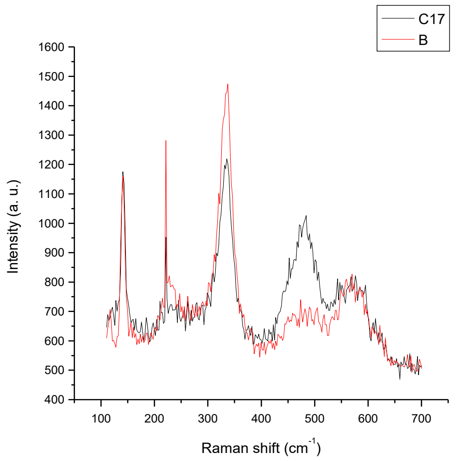

Fig. 3. Maximum intensity Raman spectra at about half of the film's thickness in a thick YBCO film before (black) and after (red) the Ar 488 nm laser irradiation.

The relative intensities of the 335 cm^{-1} and 500 cm^{-1} peaks show that the film before irradiation (black curve in Fig. 3) is strongly oriented on the *c*-axis and it is well oxygenated, and the film after irradiation (red curve in Fig. 3) is strongly oriented on the *c*-axis but not well oxygenated [4]. The intensity of the 149 cm^{-1} peak representing the Cu impurity phases becomes larger with increasing distance from the substrate (see Figs. 1 and 2), but does not change its position at the laser irradiation (see Fig. 3).

4. Conclusions

We used the pump Ar-laser (488 nm, 2 mW) of a depth profiling micro-Raman system to induce changes into a thick (1700 nm) YBCO film by heating the layers of the film for 25 minutes. The high spectral and spatial resolution of the same Raman system was used to determine the effect of the laser irradiation. In spite of a relatively small penetration depth of visible light in YBCO, of ~ 100 nm, 50 Raman spectra at different depths along the 1700 nm thick film reveal the changes in the spectral fingerprint that propagate themselves through the thickness of the film in a well established and logic manner. We discuss the laser-induced changes, most notably the oxygen loss in the affected film's layers. The maximum effect appears at a depth somewhere close to the middle of the film.

Inducing changes by laser (mostly loosing oxygen by diffusion) and studying them through Raman depth profiling before and after irradiation of YBCO films might become a new and useful approach to control the depth of these induced changes and to diagnose them with in-depth resolution better than the usual depth-of-focus and the confocal-type resolution.

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