Characterization of thin superconducting YBaCuO-films by Raman-spectroscopy

R. Feile¹, U. Schmitt¹, P. Leiderer¹, J. Schubert², and U. Poppe²

¹ Institut für Physik, Johannes-Gutenberg Universität, Mainz,
Federal Republic of Germany

² Institut für Festkörperforschung, Kernforschungsanlage Jülich,
Federal Republic of Germany

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We have investigated thin sputtered films of the high T_c material $\text{YBa}_2\text{Cu}_3\text{O}_7$ by means of Raman spectroscopy at different stages of the preparation process. We find that the films are amorphous after sputtering. The Raman spectra indicate that random polycrystalline layers, as well as crystalline layers with preferred orientation, are obtained by an additional thermal treatment.

I. Introduction

Recent investigations [1–23] have demonstrated that Raman spectroscopy is a powerful tool for the investigation of the new superconducting materials. The Raman spectra obtained by different groups display similar features, but they differ in details although the samples were produced by similar techniques and the superconducting properties are reported to be nearly the same. This has led to controversial interpretations of the observed lattice modes [3, 18, 20]. We have performed Raman experiments on sputtered YBaCuO films which were superconducting as determined by conductivity measurements. Since the thickness of the films was of the order of the penetration depth of the laser light, we assume that the observed excitations are characteristic of the bulk superconducting material.

II. Experimental procedures

The YBaCuO films were prepared by dc sputtering from a prereacted superconducting pellet with some excess BaO and CuO in order to achieve the right stoichiometry of the films. The different substrates were made of MgO, Al_2O_3 , $\text{Zr}(\text{Y})\text{O}_2$, and SrTiO_3 . The thickness of the films was typically 500–2000 nm. The as-deposited samples were not superconducting

and had to be treated thermally. After this treatment the samples were superconducting with onset temperatures between 85 K and 92 K. The width of the superconducting transition (10%–90%) in these films was 5–10 K and the critical currents of the films reached values up to 10^5 A/cm^2 . Details of the preparation process and the sample characterization will be presented elsewhere [24].

The Raman spectra have been recorded by a standard apparatus equipped with a Jobin-Yvon U 1000 double monochromator, a single channel photon counting unit, and an Ar ion laser as the light source. In order to avoid excessive heating of the film in the focus of the laser beam, we have illuminated the sample at grazing incidence or have focused the laser to a line using a cylindrical lens. In addition the laser power was reduced to about 40 mW. The samples were investigated in air at room temperature or in the vacuum chamber of a closed circuit refrigerator for the low temperature measurements.

The Raman spectra of thin films after the sputtering process usually displayed broad distributions of the scattered intensity around a frequency shift of 570 cm^{-1} , like in the spectrum of a film on a sapphire substrate, shown in Fig. 1.

After thermal treatment of the films typical Raman spectra are obtained at room temperature as it is shown in Fig. 2a for a film on Y-stabilized zirconia. It clearly displays the lines at 145, 334, 434, 499, and 600 cm^{-1} , which are also seen in other experi-

Fig. 1. Raman spectrum of a film on single crystalline SrTiO_3 substrate. The line at 332 cm^{-1} corresponds to the line at the same frequency shift in Fig. 2. The other lines are suppressed because selection rules become effective due to the preferred orientation of the film

Fig. 2. Raman spectrum of a sputtered film before thermal treatment. The broad distribution of intensity exhibits the amorphous character of the film

ments on the YBaCuO material [1–23]. When the temperature is reduced only minor changes in the spectra are observed. Figure 2b shows that the lines become narrower and shift a little. All lines move slightly to higher frequencies when the temperature is lowered, except for the excitation at 334 cm^{-1} which first stiffens and then softens on further decreasing the temperature. This is illustrated in more detail in Fig. 3. The observed temperature dependence agrees well with results on sintered samples reported in the literature [6, 12, 21, 23].

If single crystalline SrTiO_3 is used as a substrate, we observe the spectrum given in Fig. 4, which is

Fig. 3. Raman spectra of a 500 nm thick YBaCuO film a) at room temperature and b) at $T \approx 11\text{ K}$. The lines at 145, 334, 434, 499, and 600 cm^{-1} represent lattice vibrations of the superconductor. Spectrum a) has been displaced for clarity. The inset shows the spectrum of the bare zirconia substrate

Fig. 4. Temperature dependence of the five phonon modes shown in Fig. 2. The behavior of the 334 cm^{-1} line differs from that of the other excitations as it softens at temperatures below the superconducting transition. The lines are drawn as guides to the eye

dominated by a line at 332 cm^{-1} . One can further see a broad band between 450 and 620 cm^{-1} , with obviously much less developed structures than for other substrates.

We note that the relatively low background in our spectra compared to spectra obtained from sintered samples is due to the smooth surface of the films which reduces the elastically scattered stray light. This holds especially for the films on SrTiO_3 .

III. Discussion

The broad intensity distribution in the spectrum of the unannealed film (Fig. 1), resembles those spectra which we obtain when we treat sintered samples with an intense Nd—YAG laser pulse. By this procedure the material near the surface probably melts and resolidifies on a short timescale. We assume that the Raman spectrum in Fig. 1 is indicative of a broad distribution of Cu—O bond strengths in the sputtered films before annealing, possibly implying that they are amorphous.

The spectra of the thin films after thermal treatment, as shown in Fig. 2, exhibit those lines which can be found in most papers on sintered samples. The excitations between 320 and 600 cm^{-1} may be interpreted as Cu—O stretching and bond bending lattice vibrations [16, 20, 29]. This is consistent with the results of lattice dynamics calculations which will be presented elsewhere [25]. Also the Ba—O vibration at 145 cm^{-1} appears. The peak at 112 cm^{-1} is a laser plasma line. The lines at 270 and 300 cm^{-1} are due to lattice vibrations of the zirconia substrate (see inset of Fig. 2) which may be observed because the superconducting film is that thin. An excitation of the substrate at 640 cm^{-1} may also be seen in the shoulder of the 600 cm^{-1} line, evident especially in the low temperature spectra. The leaking of the substrate lines through the film indicates that we observe spectra from the entire depth of the YBaCuO layer. This means that our spectra represent bulk Raman spectra of the superconducting phase.

A line at 640 cm^{-1} (this should not be confounded with the line seen in the Zr(Y)O_2 substrates), which appears in spectra of sintered YBaCuO samples given by other authors [3, 7, 13–16, 18, 21, 23], and which has similar or sometimes even higher intensity compared to the line at 600 cm^{-1} , is not seen in our spectra. We observe that line, however, in a film which has a rather broad transition to the superconducting state after it had been exposed to humidity for some time. As this peak can also be observed in spectra of BaCuO_2 , we ascribe the 640 cm^{-1} line mainly to impurity phases originating from surface corrosion of the superconducting material [26].

The spectrum given in Fig. 4 differs at the first glance from the spectra of films presented above. Only a broad band is left where usually the lines at 434,

499, and 600 cm^{-1} appear. The excitation at 332 cm^{-1} is the only line which has its counterpart in the spectra given above. This difference can be explained by the way the films have been prepared. The films from which the spectra in Figs. 1 and 2 have been obtained were sputtered onto a cold substrate, whereas the SrTiO_3 substrate was heated during the preparation [24]. This, in addition to the fact that the single crystalline SrTiO_3 substrate has lattice constants similar to the $\text{YBa}_2\text{Cu}_3\text{O}_7$ within its basal plane, may have led to an epitaxial growth of the film. From a factor group analysis of this crystalline structure [27] it is obvious that Γ -point phonons are only observable in zz , xx , yy , xz , and yz geometry. As the spectrum shown in Fig. 4 has been measured with the polarization parallel to the film, it displays the modes with xx (or yy) symmetry. Attempts to observe the zz components have failed because of the large index of refraction of that material [28], which gives only small components of the electric field perpendicular to the film at any angle of incidence. Only when the laser was focused onto the edge of the film a small increase in intensity at 434 and 499 cm^{-1} could be observed. This is consistent with Raman measurements on single crystallites [1, 17] and indicates that the film grows epitaxially with the c -axis of the crystallites perpendicular to the surface of the SrTiO_3 substrate. The spectra given in Fig. 2 therefore suggest that the crystallites in the film on Zr(Y)O_2 have random orientation.

IV. Conclusion

We have characterized thin films of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductors by Raman spectroscopy. The results from sputtered samples before annealing indicate that they are strongly disordered. The lines found in the Raman spectra after thermal treatment can also be found in sintered samples indicating that the material is crystalline. We interpret the spectra from films on single crystalline SrTiO_3 such that the crystallites have a preferred orientation with the c -axis perpendicular to the surface. In addition arguments are presented that the line at 640 cm^{-1} which appears in the spectra of some other groups is probably not due to the superconducting phase.

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Note added

The epitaxial structure of the film on SrTiO_3 has been confirmed by channeling experiments (B. Stritzker, private communication).

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R. Feile, U. Schmitt, P. Leiderer
 Institut für Physik
 Johannes Gutenberg-Universität
 Postfach 3980
 D-6500 Mainz
 Federal Republic of Germany

J. Schubert, U. Poppe
 Institut für Festkörperforschung
 Kernforschungsanlage Jülich GmbH
 Postfach 1913
 D-5170 Jülich 1
 Federal Republic of Germany