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INVESTIGATION OF THE EPITAXY OF THIN $YBa_2Cu_3O_{7-\delta}$ FILMS

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The degree of epitaxy of thin sputtered and laser ablated films have been investigated by Raman spectroscopy. Using the selection rules for Raman scattering for the different phonons in $YBa_2Cu_3O_{7-\delta}$ the superconducting films on $SrTiO_3$ and MgO are found to be epitaxially grown with the *c*-axis perpendicular to the substrate. On ZrO_2 the films also grow with their *c*-axis perpendicular to the substrate, but with randomly oriented *a*/*b*-directions in the plane of the film.

Applications of perovskite superconductors in electronic devices will depend to a large degree on their capability to carry high current densities. As the superconductivity in those materials is strongly confined to their crystallographic *a*/*b*-plane, many laboratories focus their efforts on the production of properly oriented thin films.

Different techniques have been applied to produce thin high-T_c films, as for example thermal coevaporation of the elements in oxygen atmosphere [1], sputtering [2,3], laser ablation [4,5], and chemical vapor deposition [6,7]. Depending on which substrate is used the films grow with various morphologies which also differ in the electrical properties. The largest critical currents have been found in films on $SrTiO_3$ and MgO. On these crystals the films exhibit a preferential orientation with the *c*-axis perpendicular to the surface or even an epitaxial growth. Films deposited on Al_2O_3 and ZrO_2, however, appear randomly oriented possibly with some texture depending on the preparation conditions. Usually X-ray diffraction is used to determine the morphology of the films [1,8].

Here we report measurements with Raman spectroscopy, a method which has also been successfully applied to characterize high-T_c films [9]. Not only different impurity phases could be distingushed from the pure superconducting phase [10], but also a preferred *c*-axis orientation of films could be established. This is possible because of the distinct selection rules for Raman scattering from the optical phonons in these superconductors [10,11]. Figure 1 gives the spectra of films on $SrTiO_3$, MgO and ZrO_2.

The scattering from the phonon mode near 500 cm^{-1} is described by the Raman tensor of the form

$$\alpha = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & c \end{pmatrix}.$$

This means that the intensity of this mode $I = |(E_s \alpha E_i)|^2$ is zero if the electric field vectors of the incident and scattered light E_i and E_s are polarized in the *a*/*b*-plane of the crystal. Therefore the disappearance of this 500 cm^{-1} excitation in Raman spectra of superconducting $YBa_2Cu_3O_{7-\delta}$ films has been interpreted as to indicate an orientation of the high-T_c crystallites with their *a*/*b*-plane parallel to the substrate.

The other intensively studied phonon [10,11] is the 335 cm^{-1} A_{1g} phonon. Its Raman tensor

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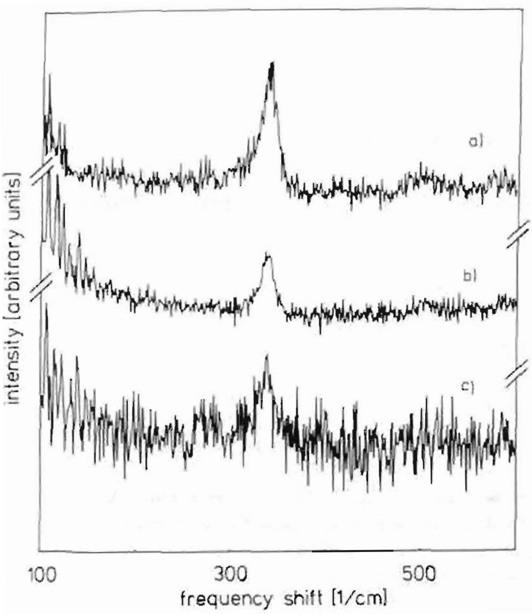

Fig. 1. Depolarized Raman spectra of thin $YBa_2Cu_3O_{7-\delta}$ films on sputtered $SrTiO_3$ (a), and laser ablated on MgO (b) and ZrO_2 (c) substrates.

$$\alpha=\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

indicates that it appears in spectra where E_i and E_s lie within the a/b-plane. Since this mode is an out-of-plane motion of the oxygen in the almost quadratic Cu–O layers, the two components of the Raman tensor are related to each other: $b\approx -a$ (therefore this mode is often called a pseudotetragonal B_{1g} mode). Thus, the depolarized scattering due to this phonon vanishes if the polarization of the laser light bisects the a/b-plane. We have used this characteristic feature of the 335 cm^{-1} phonon to measure the degree of epitaxy of $YBa_2Cu_3O_{7-\delta}$ films on $SrTiO_3$, MgO and Y-stabilized ZrO_2.

The Raman apparature described elsewhere [9] has been modified to allow a well defined backscattering geometry. The power of the Ar-ion laser (514 nm) in the focus of about 30 μm in diameter at the sample was 40 mW. The substrate with the $YBa_2Cu_3O_{7-\delta}$ film was mounted on a rotational table whose axis was carefully aligned along the optical axis of the Raman spectrometer so that always the same spot of the film remained in the focus during the rotation.

With this procedure we investigated the sputtered $YBa_2Cu_3O_{7-\delta}$ film on $SrTiO_3$ crystal. The absence of the 500 cm^{-1} phonon mode in the depolarized Raman spectra (fig. 1(a)) indicates the orientation of the c-axis perpendicular to the substrate. Figures 2(a–c) show the intensity of the 335 cm^{-1} phonon when the film is rotated around an axis perpendicular to the film at a fixed monochromator setting. Similar to the behavior for a single crystal the modulation of the intensity with the rotation angle Φ follows a $\cos^2(2\Phi)$ low. This means that the film within the laser focus is oriented not only with respect to the c-axis, but also with its a/b-directions over the hole

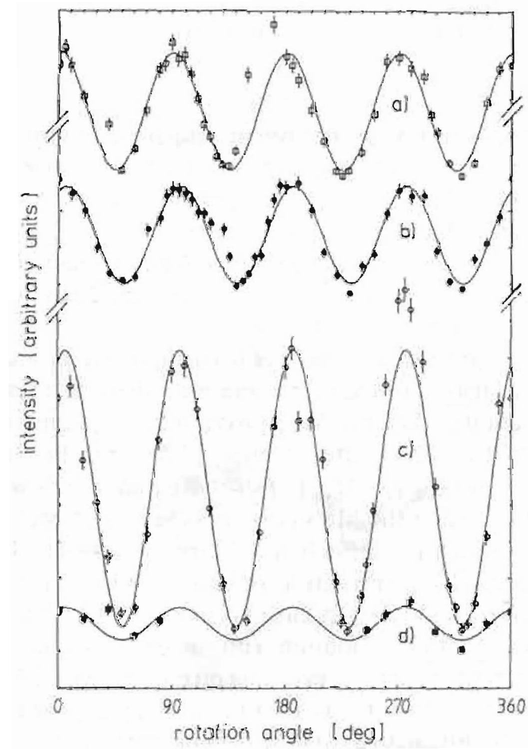

Fig. 2. Modulation of the 335 cm^{-1} phonon intensity in a sputtered $YBa_2Cu_3O_{7-\delta}$ film on a $SrTiO_3$ substrate as a function of the rotation of the film around the surface normal by an angle Φ. Three separated spots on the film spaced several mm apart have been investigated (a, b, c). For comparison, the lowest trace (d) shows the background intensity at 400 cm^{-1} (taken at the same film position as trace (c)).

focal area. The intensity maxima indicate the (110)- and/or ($\bar{1}$10)-directions (a distinction between a and b could not be made here). The lines are the result of a fit to $I(\Phi)=a\cos^2(2\Phi+\Delta)+B$. The value for Δ is the offset of the angular reading measured with respect to the (110)-direction.

The background B we consider to consist of two contributions: one from the 335 cm^{-1} phonon isotropically oriented crystallites and another one from a broad spectrum of electronic excitations [12]. In order to separate the two, we have set the spectrometer to a structureless region in the spectrum around 400 cm^{-1} and repeated the procedure for the same spot as fig. 2(c). The result is given in fig. 2(d). The small modulation in phase with the intensity of the 335 cm^{-1} phonon may be due to the electronic contribution of the same symmetry as the phonon (pseudotetragonal B_{1g}). By subtracting the electronic contribution from the phonon intensity we can estimate that 90% of the $YBa_2Cu_3O_{7-\delta}$ film within the laser spot is a/b oriented.

We now want to address the question of whether the film exhibits long range order across the substrate over distances much larger than the diameter of the focus. For this we have performed the same measurement for various positions on the film separated from the first spot by several millimeters. Two examples are included in figs. 2(a, b). Obviously these modulations are in phase with that of the first experiment. We therefore conclude that large regions of the film on the $SrTiO_3$ substrate have grown epitaxially.

The results obtained for the film on the $SrTiO_3$ substrate prepared by laser ablation are shown in figs. 3(a–c). The ratio of a/b-ordered to random oriented crystallites was reduced to 65% as can be derived from the modulations at 335 cm^{-1} and 400 cm^{-1} on the same spot (figs. 3(b) and 3(c)).

Similar modulations are obtained from $YBa_2Cu_3O_{7-\delta}$ films grown on MgO substrates.

By contrast, films prepared by laser ablation on ZrO_2 substrates do not display any periodic intensity variation of the 335 cm^{-1} line when the sample is rotated. Therefore these films consist of crystallites which are not preferentially oriented with respect to their a/b-axes. Nevertheless, the c-axes of the crystallites are well oriented perpendicular to the sub-

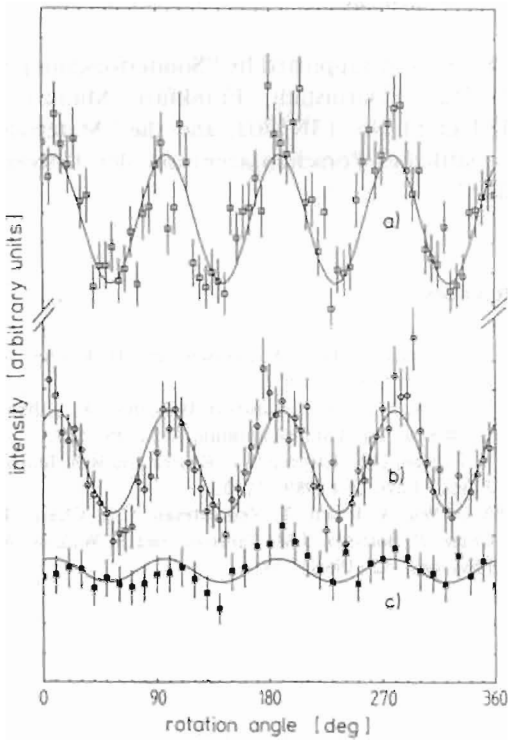

Fig. 3. Modulation of the 335 cm^{-1} phonon intensity in a laser ablated $YBa_2Cu_3O_{7-\delta}$ film on an $SrTiO_3$ substrate on rotation of the film around the surface normal (a, b) and for the background at 400 cm^{-1} (c) (b and c are taken from the same position on the film).

strate, as is evident from the absence of the 500 cm^{-1} phonon line in fig. 1(c).

Conclusions

In conclusion we have demonstrated that using the specific Raman selection rules for the pseudotetragonal B_{1g} phonon in the high-T_c superconductors, detailed information on the morphology of the films can be obtained. In particular it is possible to distinguish epitaxial growth from random a/b orientation. A systematic study of the different preparation conditions is underway.

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