X-ray diffraction analysis of YBaCuO ultra-thin film growth

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Abstract
The initial growth stages of YBaCuO films deposited by sputtering in the thickness range of 0.6 to 5 nm on (100) SrTiO$_3$ and MgO substrates have been studied by standard X-ray diffraction. A comparison of film thicknesses estimated from line breadth with the nominal values indicates layered growth in a unit cell by unit cell mode on SrTiO$_3$, while island growth occurs on MgO until full coverage is reached at 5 nm. Pseudomorphic growth appears to be present on both substrates but restricted to different film thicknesses, i.e., about 4 nm on SrTiO$_3$ and one unit cell on MgO. In films with thicknesses up to two unit cells the YBaCuO “123” phase coexists with oxides of the cations, an appearance which also was observed in the BiSrCaCuO “2223” phase. The growth characteristics are in agreement with observations made by high resolution backscattering on similar films.

Keywords: YBaCuO thin films; Film growth

1. Introduction

High epitaxial growth quality, determining also the transport properties, is an essential prerequisite for the application of thin films of the high temperature superconductors. The initial stages of growth at the film substrate interface may ultimately determine the growth and properties of thicker films, but are essential for the performance of ultra-thin films consisting of a few unit cells in thickness only. Such films are required for small scale applications like the construction of bolometers or to serve as channels in superconducting field effect transistors. Also from the basic point of view growth studies at the initial stage are of interest and quite frequently have been performed by RHEED or AFM.

In this contribution we have applied conventional X-ray diffraction in the symmetric Bragg case to study the growth of YBaCuO films with thicknesses in the range of 0.6–5 nm on (100) SrTiO$_3$ and MgO substrates. We have compared the results to previous investigations made by high resolution Rutherford backscattering (RBS) on similar films [1,2] and thus were able to elucidate the potentials of standard X-ray diffraction which so far has been used less frequently for growth studies [3,4].

2. Experimental

The YBaCuO films were deposited by sputtering employing the inverted cylindrical magnetron device [5]. The deposition parameters were those for the usual production of thicker c-axis films. The nominal film thickness was obtained from the calibrated deposition rate (0.1 nm/s) and deposition time and was controlled by RBS. The films were covered with 2–3 nm thick amorphous protection layer deposited at RT. The diffraction measurements were performed with CuK$_\alpha$$_1$ radiation supplied by a rotating anode X-ray generator operated at 8 kW on a two axes goniometer. We have measured $\theta$–2$\theta$ scans and rocking curves reflecting the mosaic distributions in the films with counting times per step up to 150 s depending on film thickness.

3. Results

The measurements revealed that for epitaxial YBaCuO films conventional X-ray diffraction is sufficiently sensitive to deliver diffraction signals from samples with thicknesses down to one unit cell (uc) in c-axis direction. Examples of diffraction diagrams for films on SrTiO$_3$ are displayed in Fig. 1 for three thicknesses in the range of the (005) line. For the 2 uc and 3 nm thick films the (005) peak is well resolved above the background such that a clear determination of peak position and breadth is possible. For the 1 uc film it is, however, smeared out and the
relevant parameters can be only estimated. On MgO the (005) line overlaps partially with the (200) substrate line, but in this case the detached (003) peak also for a 1 uc thick film as shown in Fig. 2 can be used for analysis.

Neglecting the influence of possible local strains on the line breadth we applied the Scherrer equation \( \Delta 2\theta = K \cdot \lambda / L \cos \theta \). \( \Delta \) is the line breadth, \( L \) the mean dimension of the crystallites, and \( K \) a constant close to unity) for grain size determination which in the case of epitaxial single crystalline films corresponds to the film thickness. This procedure appeared justified because in an alternative attempt of a separate determination of grain size and strain it turned out that the microstrains are small. In this attempt we performed plots after Halder and Wagner [6] where \( \Delta / \tan \theta \) is plotted vs. \( \Delta / (\tan \theta \sin \theta) \) delivering a straight line whose slope yields the grain size and the axial section value the strain. The plots were performed for nominally 5 nm thick films where up to five resolved (00l) lines were available for analysis [7]. The results for the film thickness were 5.2 nm and 5.4 nm on \( \text{SrTiO}_3 \) and MgO, respectively, which is close to the nominal values. The strain for the film on \( \text{SrTiO}_3 \) was 0.35%, i.e., consequently small; on MgO the axial section value of the Halder-Wagner plot was negative and due to the larger scatter of the data had a larger error but absolutely the value was in the same range as on \( \text{SrTiO}_3 \).

Concerning the film thickness as estimated from the Scherrer formula for values below 5 nm a distinct difference was observed for the two substrates. On \( \text{SrTiO}_3 \) the measured values were close to or slightly above the nominal ones, e.g., 1.5 nm, 2.6 nm and 3.1 nm for nominally 1 uc, 2 uc and 3 nm thick films, respectively. In contrast, on MgO the measured thicknesses were larger than the nominal values. The minimum value of 3.4 nm was determined for a nominally 1 uc thick film and not until thicknesses around 5 nm did the experimental values agree with the nominal ones as shown before in the Halder-Wagner plots. The latter plots were less reliable for thickness determination of the thinner films because here usually only two points were available. Nevertheless, the results also at least qualitatively underlined the different behaviour on the different substrates.

The minimum thickness value of about 3.4 nm on MgO indicates incomplete substrate coverage and points to island growth. It is in perfect agreement with the observations in the backscattering experiments where irrespective of the film thickness at least a 3 uc pile up with different percentages of coverage on the various levels has been
determined [1]. The agreement of nominal and experimental thickness values for films on SrTiO$_3$ in contrast to the observations on MgO shows that almost complete coverage is achieved already after deposition of a 1 uc thick film again in agreement with high resolution RBS measurements where 100% coverage and uniform film thickness was directly seen for films deposited with thicknesses of full numbers of unit cells. Thus, concerning the growth modes we conclude that on SrTiO$_3$, the growth of an additional unit cell layer is initiated only after the preceding one has been accomplished, i.e., in principle the Stranskí–Krástanov growth mode takes place with one unit cell block as a growth layer. On MgO the initial stages of nucleation are described by island formation, i.e., nucleation proceeds in the Volmer–Weber growth mode.

Though with films around 5 nm thickness full coverage is achieved on both substrates and the initial growth stages appear completed, the different growth modes probably influence the thickness homogeneity of the films which was superior on SrTiO$_3$. We draw this conclusion from Laue oscillations observed for the film on the latter substrate. Two well resolved maxima appeared aside the (005) peak as expected for a 4 uc thick film, since theory [8] predicts $N$=2 maxima with $N$ being the number of unit cells building up a film in thickness. The Laue oscillations deliver a further possibility of independent film thickness determination yielding in this case a value of 5.5 nm which we consider to be still in accordance with the nominal value. The good film homogeneity leading to Laue oscillations also is an indication that spiral growth has not yet been initiated at this film thickness. On MgO Laue oscillations at the (005) line were not resolved which partly may be due to the higher background in the vicinity of the substrate line, but mainly is thought to be a consequence of a rougher surface morphology arising from the Volmer–Weber growth mode.

In channelling experiments for films on SrTiO$_3$, an abrupt increase of the minimum yield values at a critical film thickness was interpreted as a transition from strained pseudomorphic growth for thinner films to strain release by defect incorporation for thicker films above the critical value [2]. The $a$ and $b$ axes lattice constants of the YBaCuO "123" structure which are accommodated in the film plane for $c$-axis growth both are smaller than the lattice constant of SrTiO$_3$. Therefore, from simple matching arguments, tensile strain could be expected in pseudomorphic films leading to a shrinkage of the $c$-axis lattice constant which should be detected in the diffraction experiments. For 5 nm thick films which is above the critical value we determined $c$-values on both substrate materials in the range of 1.168–1.170 nm which is close to bulk value, i.e., strain was released. For thinner films a reliable determination of $c$ was hampered by the very limited number of lines and the dependence of the $c$-values on the diffraction angle. Nevertheless, by comparison to the angle dependence determined for thicker films (100–200 nm) or single crystals we were able to estimate the lattice constant for 3 nm and 3 uc thick films on SrTiO$_3$ and MgO, respectively. While for the film on SrTiO$_3$ the value was considerably reduced (0.5% effect), that on MgO rather corresponded to the bulk value. This for SrTiO$_3$ is in accordance with the channelling results and for both substrates with the different growth modes discussed before. For even thinner films the situation is somewhat puzzling. A 2 uc film on SrTiO$_3$ revealed an enhanced value of $c$ which should not occur according to the previous argument but may be due to the presence of other oxides in the film which will be discussed later. From the position of the only resolved (003) line of a 1 uc film on MgO, however, rather a considerable contraction of $c$ was estimated which would indicate pseudomorphic growth. This is not excluded on MgO, but if it exists the critical film thickness as compared to SrTiO$_3$ should be reduced due to the larger lattice misfit. In fact, Terashima et al. [9] reported a value of about 1.2 nm deduced from RHEED experiments.

We in addition have measured rocking curves on films with different thickness and found an increase of the mosaic spread with increasing film thickness. The most obvious effect, however, was a change in the shape of the total mosaic distributions as displayed in Fig. 3 for three thicknesses on MgO. While the curve for the 1 uc film is narrow with steep edges, those of the thicker films are wider with tails extending to larger angles. Though this appearance does not prove pseudomorphic growth, it is consistent with a transition from such a mode to grain growth with dislocation incorporation leading to wider mosaic distributions.

A surprising feature in the X-ray diffraction diagrams of films with thicknesses in the range of 0.5–2 uc were some faint but sharp peaks which partly can be seen also in Figs. 1 and 2. The assignment of the peaks is not unique but most probably they arise from oxides of the cations in YBaCuO like BaO, CuO and Y$_2$O$_3$. The peaks disappeared for larger thicknesses which suggests that the oxides coexist with the “123” phase only in the very initial stages of phase formation and before like in the 0.5 uc thick films where signals from the oxides but not from the “123” phase could be detected. In this context it is interesting to note that Hirata et al. [10] reported Cu$_2$O formation before YBaCuO nucleation from RHEED experiments. Fan and Somer [4] also observed oxides (CuO, Y$_2$O$_3$) in ultra-thin films but these appeared to grow with increasing film thickness in contrast to our observations. The breadth of our oxide peaks suggests a much larger extension than the nominal film thickness and it is not clear how they are consumed in further film growth. The observations, however, appear of a more general nature, since we observed sharp oxide lines also in the background of broad lines of the “2223” phase of BiSrCaCuO as demonstrated by the diffraction diagram displayed in Fig. 4 for a 2 uc thick film. In this case
accompanying AFM measurements directly revealed extended oxide outgrowth out of a very smooth "2223" matrix.

4. Conclusions

Standard X-ray diffraction measurements in the symmetric mode on ultra-thin YBaCuO films proved to be sufficiently sensitive to discriminate between different growth modes with unit cell by unit cell layer growth on SrTiO$_3$ and island formation on MgO. The observations are in agreement with previous high resolution RBS measurements on similar films. Conclusions with respect to strain in the films and pseudomorphic growth from line positions and lattice constant determination in 1 to 2 uc thick films suffer from lack of precision and have to be considered as preliminary. Here, the breadth of rocking curves and on MgO especially their shape are indicative for pseudomorphic growth for 1 uc thick films also in agreement with Bauder et al. [11] who reported pseudomorphic island growth up to thicknesses of 1.5 nm. The coexistence of cationic oxides with the "123" phase in the initial stages of nucleation and their possible influence on the growth modes is intriguing and deserves further investigations.

References


